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A 2:1 Ionic Complex of 2-Hydroxy-5-methyl-1,3-benzenedicarbaldehyde and Diaza-18-crown-6*

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Abstract. $C_{12}H_{28}N_2O_4^{2+}.2C_9H_7O_3^-$, $M_r = 590{\cdot}68$, triclinic, $P\bar{1}$, $a = 7{\cdot}412\,(1)$, $b = 8{\cdot}763\,(1)$, $c = 12{\cdot}688\,(1)$ Å, $\alpha = 72{\cdot}44\,(1)$, $\beta = 85{\cdot}95\,(1)$, $\gamma = 76{\cdot}34\,(1)°$, $V = 763{\cdot}4\,(1)$ Å^3, $Z = 1$, $D_x = 1{\cdot}285$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}90$ cm^{-1}, $F(000) = 316$, $T = 295$ K, $R = 0{\cdot}0428$ for 1530 observed reflections. The protons of two planar 2-hydroxy-5-methyl-1,3-benzenedicarbaldehydes are transferred to the two 'diaza' N atoms of the crown. The C(2)—O(2)$^-$ distance is reduced to 1·287 (3) Å and an N—H···O(2) hydrogen bond is formed, N···O(2) = 2·575 (3) Å, N—H···O(2) = 167 (2)°. The diaza-18-crown-6 dication adopts a conformation analogous to the D_{3d} conformation of 18-crown-6.

Experimental. The complex was prepared by mixing diaza-18-crown-6 and the dialdehyde in a 1:2 ratio in a minimum quantity of ethyl acetate. After refluxing for several hours the material was filtered, cooled and the crystals collected. Recrystallization from ethyl acetate produced transparent colorless crystals. A crystal of dimensions 0·20 × 0·275 × 0·30 mm was mounted on a Nicolet $R3m/\mu$ update of a $P2_1$ diffractometer, data collected ($3 \le 2\theta \le 45°$) in the Wyckoff mode (2θ fixed, ω varied) using a variable scan rate and graphite-monochromated Mo $K\alpha$ radiation; lattice parameters from a least-squares refinement of 25 reflections ($37{\cdot}1 \le 2\theta \le 41{\cdot}88°$), angles measured by a centering routine, no systematic absences and Laue symmetry $\bar{1}$ consistent with space group $P\bar{1}$; monitored reflections $\bar{1}06$ and 243 showed only statistical variations in intensities, 1995 independent reflections measured ($-7 \le h \le 7$, $-8 \le k \le 8$, $0 \le l \le 13$), $1530 \ge 3\sigma(I)$, Lorentz–polarization corrections applied, ψ-scan empirical absorption correction (transmission factors 0·917 to 0·959); structure solved by direct methods; block-cascade anisotropic refinement, H atoms located in difference map and refined isotropically; $R = 0{\cdot}0428$, $wR = 0{\cdot}0415$ for 274 parameters, $R(\text{all}) = 0{\cdot}0606$; $S = 1{\cdot}393$, $(\Delta/\sigma)_{\max} = 0{\cdot}015$, largest peaks in the final difference map of $-0{\cdot}21$ and $+0{\cdot}15$ e Å^{-3}; function minimized $\sum w(|F_o| - |F_c|)^2$ where $w = [\sigma^2(F_o) + 0{\cdot}00038F_o^2]^{-1}$.

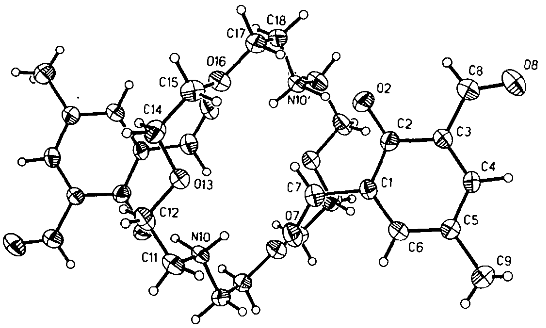

Fig. 1. Drawing of the title complex. Thermal ellipsoids are drawn at the 35% probability level. H atoms are represented by spheres of arbitrary size.

Table 1. *Atomic coordinates* (×10^4) *and equivalent isotropic thermal parameters* (Å^2×10^3)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	2173 (3)	4238 (3)	2464 (2)	44 (1)
C(7)	2066 (4)	3971 (4)	3650 (2)	55 (1)
O(7)	2311 (3)	2638 (2)	4344 (1)	66 (1)
C(2)	1947 (3)	5858 (3)	1724 (2)	46 (1)
O(2)	1600 (3)	7148 (2)	2057 (1)	68 (1)
C(3)	2153 (3)	5983 (3)	579 (2)	47 (1)
C(8)	1955 (4)	7588 (3)	−230 (2)	71 (1)
O(8)	2113 (3)	7843 (2)	−1218 (2)	96 (1)
C(4)	2544 (4)	4587 (3)	235 (2)	57 (1)
C(5)	2757 (4)	3021 (3)	950 (2)	56 (1)
C(9)	3185 (5)	1520 (3)	550 (2)	92 (2)
C(6)	2581 (3)	2897 (3)	2054 (2)	49 (1)
N(10)	855 (3)	1936 (2)	6584 (1)	49 (1)
C(11)	2732 (4)	1476 (3)	7075 (2)	62 (1)
C(12)	3123 (4)	2888 (3)	7380 (2)	61 (1)
O(13)	2995 (2)	4235 (2)	6413 (1)	57 (1)
C(14)	3183 (5)	5678 (3)	6647 (2)	56 (1)
C(15)	3378 (4)	6957 (3)	5595 (2)	57 (1)
O(16)	1639 (2)	7614 (2)	5049 (1)	54 (1)
C(17)	1717 (4)	8844 (3)	4038 (2)	59 (1)
C(18)	−177 (4)	9453 (3)	3564 (2)	58 (1)

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* 1,7,10,16-Tetraoxa-4,13-diazacyclooctadecane.

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Table 2. *Bond lengths* (Å) *and valence angles* (°)

C(1)—C(7)	1·450 (3)	C(1)—C(2)	1·425 (3)
C(1)—C(6)	1·387 (3)	C(7)—O(7)	1·214 (3)
C(2)—O(2)	1·287 (3)	C(2)—C(3)	1·424 (3)
C(3)—C(8)	1·452 (3)	C(3)—C(4)	1·381 (4)
C(8)—O(8)	1·207 (3)	C(4)—C(5)	1·378 (3)
C(5)—C(9)	1·507 (4)	C(5)—C(6)	1·372 (3)
N(10)—C(11)	1·481 (3)	N(10)—C(18′)	1·486 (3)
C(11)—C(12)	1·496 (4)	C(12)—O(13)	1·413 (2)
O(13)—C(14)	1·423 (4)	C(14)—C(15)	1·485 (3)
C(15)—O(16)	1·417 (3)	O(16)—C(17)	1·413 (2)
C(17)—C(18)	1·480 (4)	C(18)—N(10′)	1·486 (3)

C(7)—C(1)—C(2)	120·6 (2)	C(7)—C(1)—C(6)	119·4 (2)
C(2)—C(1)—C(6)	120·0 (2)	C(1)—C(7)—O(7)	125·3 (3)
C(1)—C(2)—O(2)	122·8 (2)	C(1)—C(2)—C(3)	116·2 (2)
O(2)—C(2)—C(3)	121·1 (2)	C(2)—C(3)—C(8)	119·7 (2)
C(2)—C(3)—C(4)	120·4 (2)	C(8)—C(3)—C(4)	119·8 (2)
C(3)—C(8)—O(8)	125·6 (3)	C(3)—C(4)—C(5)	123·4 (2)
C(4)—C(5)—C(9)	122·3 (2)	C(4)—C(5)—C(6)	116·2 (2)
C(9)—C(5)—C(6)	121·5 (2)	C(1)—C(6)—C(5)	123·8 (2)
C(11)—N(10)—C(18′)	114·8 (2)	N(10)—C(11)—C(12)	110·1 (2)
C(11)—C(12)—O(13)	108·3 (2)	C(12)—O(13)—C(14)	111·9 (2)
O(13)—C(14)—C(15)	109·4 (2)	C(14)—C(15)—O(16)	109·7 (2)
C(15)—O(16)—C(17)	113·0 (2)	O(16)—C(17)—C(18)	107·8 (2)
C(17)—C(18)—N(10′)	109·7 (2)		

Computer programs for Desktop 30 Microeclipse and Nova 4/C configuration (Nicolet Instrument Corporation, 1986); scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Table 1 lists atomic positional parameters and U_{eq} values while Table 2 gives bond lengths and bond angles. Fig. 1 is a drawing of the title compound.*

Related literature. The interactions between crown macrocycles and organic host molecules have been of increasing interest during the past decade and have been the subject of several reviews (Vögtle, Sieger & Müller, 1981; Vögtle, Müller & Watson, 1984; Atwood, Davies & MacNicol, 1984). The structures of ionic complexes of diaza-18-crown-6 with tropolone and 4-hydroxy-3-methoxybenzaldehyde have been reported (Watson, Vögtle & Müller, 1988). The conformations of complexed crown ethers in the solid state have been investigated and are the subject of a number of reports (*e.g.* Elbasyouny *et al.*, 1983; Watson, Galloy, Grossie, Vögtle & Müller, 1984).

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* Lists of H-atom coordinates, anisotropic thermal parameters, torsion angles and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44923 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

ATWOOD, J. L., DAVIES, J. E. D. & MACNICOL, D. D. (1984). Editors. In *Inclusion Compounds*, Vols. I–III. London: Academic Press.

ELBASYOUNY, E., BRUGGE, H. J., VON DEUTEN, K., DICKEL, M., KNÖCHEL, A., KOCH, K. U., KOPF, J., MELZER, D. & RUDOLF, G. (1983). *J. Am. Chem. Soc.* **105**, 6568–6577.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Nicolet Instrument Corporation (1986). *SHELXTL* for Desktop 30 (Microeclipse), PN-269-1040340, April.

VÖGTLE, F., MÜLLER, W. M. & WATSON, W. H. (1984). *Top. Curr. Chem.* **125**, 131–164.

VÖGTLE, F., SIEGER, H. & MÜLLER, W. M. (1981). *Top. Curr. Chem.* **98**, 107–161.

WATSON, W. H., GALLOY, J., GROSSIE, D. A., VÖGTLE, F. & MÜLLER, W. M. (1984). *J. Org. Chem.* **49**, 347–357.

WATSON, W. H., VÖGTLE, F. & MÜLLER, W. M. (1988). *Acta Cryst.* C**44**, 141–145.

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Structure of (*Z*)-Methyl 3-[(*E*)-(2-Cyano-1-phenylethylidene)amino]-3-methylthiopropenoate

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Abstract. $C_{14}H_{14}N_2O_2S$, $M_r = 242{\cdot}277$, triclinic, $P\bar{1}$, $a = 8{\cdot}019\ (3)$, $b = 9{\cdot}858\ (3)$, $c = 10{\cdot}295\ (3)$ Å, $\alpha = 115{\cdot}26\ (3)$, $\beta = 99{\cdot}24\ (3)$, $\gamma = 90{\cdot}63\ (2)°$, $V = 723{\cdot}6\ (5)$ Å^3, $Z = 2$, $D_m = 1{\cdot}259$, $D_x = 1{\cdot}111$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}21$ mm^{-1}, room temperature, $F(000) = 288$, final $R = 0{\cdot}065$ and $wR = 0{\cdot}085$ for 3318 observed reflections. There is no electronic conjugation in the molecular chain with a

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