similar disorder was observed in $[Mn(H_2O)_6](ClO_4)_2.18$-crown-6 (Vance, Holt, Varie & Holt, 1980). The distances of Table 3 indicate a network of hydrogen bonding between polyether O atoms and the $[Co(H_2O)_6]$ group.

The molecule of acetone shows normal bond angles and distances. An infrared spectrum shows a peak at 1691 cm^{-1}, a shift of 22 cm^{-1} to lower frequency as compared to the spectrum of free acetone, confirming the H(302)—O(22) hydrogen bond indicated in Table 3.

The 18-crown-6 thus fails to form the direct Co—O(polyether) bonds proposed by Su & Weiher (1968).

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Structure of Hexaaquamanganese(II) Perchlorate–18-Crown-6*

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Abstract. $[Mn(H_2O)_6](ClO_4)_2.C_{12}H_{24}O_6$, monoclinic, $P2_1/c$, $a = 14.099$ (5), $b = 10.619$ (6), $c = 17.956$ (8) Å, $\beta = 91.37$ (3)°, $V = 2688$ (2) Å^3, $Z = 4$, $D_m = 1.62$ (1), $D_c = 1.55$ Mg m^{-3}, μ(Mo $K\alpha$) = 0.80 mm^{-1}. Least-squares refinement of diffractometer data (1593 observed reflections) to $R_1 = 7.5\%$ shows Mn with an octahedral coordination sphere of water molecules. Hydrogen bonding appears to tether the hexaaquamanganese cation between two crystallographically nonequivalent crown ether rings.

Introduction. Transition-metal complexes with crown ethers have received little attention in the literature (Vance, Holt, Pierpont & Holt, 1980; and references therein). We have determined the structures of a series of these complexes to examine structural consequences of change of ring size and metal ion.

The title compound was prepared by addition of a dilute acetic acid solution of hexaaquamanganese(II) perchlorate to a dilute acetic acid solution of 18-crown-6 (1:1). Colorless crystalline rods were formed on evaporation. These were observed to decompose in air. (Analysis: calculated for $C_{12}H_{36}Cl_2MnO_{20}$: Mn, 8.77; C, 23.02; H, 5.79; Cl, 11.32%; found: Mn, 8.55; C, 22.95; H, 5.80; Cl, 11.27%.)

A single crystal of average diameter 0.21 mm and 0.54 mm in length was mounted in a glass capillary. A Syntex $P\bar{1}$ four-circle automated diffractometer with a pulse-height analyzer and graphite-monochromatized radiation were used for data collection. Least-squares refinement of the angular coordinates of 15 independent reflections (4.5° < 2θ < 17.9°) allowed determination of cell constants and standard deviations. Room-temperature measurement of 2705 reflections ($2\theta_{max} = 40°$) using a $\theta/2\theta$ scan produced 1593 observed data [$I > 3\sigma(I)$]. A fixed scan rate of 3° min^{-1} and a background to scan time ratio of 0.8:1 were employed. The intensities of three check reflec-

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tions were remeasured after every 100 reflections. Corrections for decay, Lorentz and polarization effects, and absorption (transmission factors: max. 0·871, min. 0·866) were applied.

The Mn atom was located by heavy-atom methods. Subsequent least-squares refinement [function minimized: $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma(F_o)^2$] of positional, thermal and scale parameters, followed by a difference Fourier synthesis, allowed location of the remaining non-hydrogen atoms. The asymmetric unit contains one-half of the atoms of each of two crystallographically non-equivalent 18-crown-6 rings. Final refinement of anisotropic thermal parameters, positional parameters and the scale factor gave final discrepancy indices: $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o| = 0{\cdot}075$, $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0{\cdot}079$. Atomic scattering factors (Cromer & Mann, 1968) for Mn^{2+} and Cl were corrected for the real and imaginary parts of anomalous dispersion (*International Tables for X-ray Crystallography*, 1974). The XRAY 76 system was used for all calculations (Stewart, 1976).*

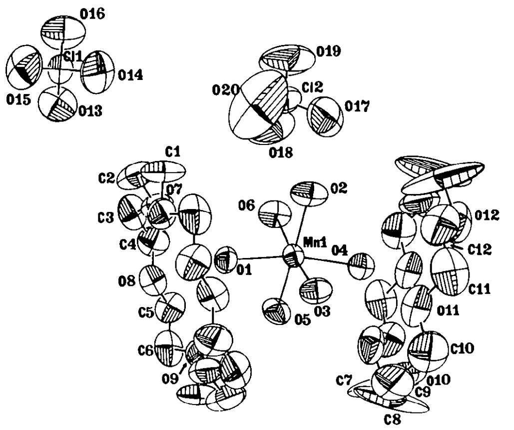

Fig. 1. $[Mn(H_2O)_6](ClO_4)_2$. 18-crown-6.

Table 1. *Final positional parameters and standard deviations* (×10⁴)

	x	*y*	*z*
Mn(1)	7494 (1)	224 (2)	538 (1)
O(1)	5986 (5)	−62 (8)	462 (4)
O(2)	7674 (6)	−977 (7)	1546 (4)
O(3)	7646 (6)	−1580 (8)	−63 (4)
O(4)	9003 (6)	469 (8)	357 (4)
O(5)	7280 (6)	1462 (8)	−430 (4)
O(6)	7359 (7)	1797 (7)	1306 (5)
C(1)	4590 (16)	−1082 (21)	1925 (10)
C(2)	4108 (15)	106 (23)	1922 (10)
O(7)	4613 (8)	949 (13)	1424 (6)
C(3)	4138 (13)	2146 (21)	1361 (12)
C(4)	4667 (14)	2978 (18)	849 (11)
O(8)	4586 (7)	2473 (9)	118 (6)
C(5)	5050 (12)	3351 (16)	−386 (11)
C(6)	4937 (12)	2794 (18)	−1152 (12)
O(9)	5508 (7)	1681 (11)	−1199 (6)
C(7)	9642 (20)	1424 (26)	−1765 (14)
C(8)	488 (22)	−142 (28)	1955 (16)
O(10)	400 (9)	830 (16)	1474 (6)
C(9)	914 (15)	2004 (25)	1561 (12)
C(10)	388 (15)	2905 (19)	1035 (14)
O(11)	492 (7)	2477 (10)	304 (8)
C(11)	20 (14)	3337 (16)	−236 (14)
C(12)	34 (15)	2742 (23)	−975 (13)
O(12)	9431 (9)	1696 (14)	−1045 (8)
Cl(1)	2509 (3)	335 (4)	3801 (2)
O(13)	2450 (8)	1310 (11)	3278 (6)
O(14)	3295 (9)	−409 (11)	3663 (7)
O(15)	1710 (10)	−389 (12)	3763 (7)
O(16)	2609 (10)	905 (11)	4511 (7)
Cl(2)	7483 (4)	658 (5)	3254 (2)
O(17)	8256 (11)	170 (16)	2926 (8)
O(18)	7297 (13)	1779 (16)	2883 (8)
O(19)	7597 (13)	986 (15)	3967 (8)
O(20)	6781 (16)	−93 (21)	3103 (14)

Fig. 1 identifies the atoms of the asymmetric unit based on the atomic coordinates of Table 1.

Discussion. The Mn^{II} ion retains its coordination sphere of six water molecules in the presence of 18-crown-6. The octahedron is distorted from ideal geometry with 'right angles' of 83·7 (3)–98·4 (3)°. Mn^{II}—O distances range from 2·150 (8)–2·224 (8) Å with an average of 2·189 Å; this is in good agreement with the average of 2·18 Å reported for Mn^{II}—O(water) in $[Mn(H_2O)_5NO_3]^+$.18-crown-6.NO_3^-.H_2O (Knöchel, Kopf, Oehler & Rudolph, 1978).

Table 2. *Selected distances* (Å) *and angles* (°)

$[Mn(H_2O)_6]^{2+}$			
Mn(1)—O(1)	2·150 (8)	Mn(1)—O(4)	2·175 (8)
Mn(1)—O(2)	2·224 (8)	Mn(1)—O(5)	2·194 (8)
Mn(1)—O(3)	2·211 (8)	Mn(1)—O(6)	2·178 (8)
18-Crown-6 (ring centered at ½,0,0)			
C(1)—C(2)	1·43 (3)	O(8)—C(5)	1·46 (2)
C(2)—O(7)	1·46 (2)	C(5)—C(6)	1·50 (3)
O(7)—C(3)	1·44 (2)	C(6)—O(9)	1·43 (2)
C(3)—C(4)	1·49 (3)	O(9)—C(1)′	1·45 (2)
C(4)—O(8)	1·42 (2)		
C(1)—C(2)—O(7)	108 (2)	O(8)—C(5)—C(6)	106 (1)
C(2)—O(7)—C(3)	111 (1)	C(5)—C(6)—O(9)	109 (1)
O(7)—C(3)—C(4)	109 (2)	C(6)—O(9)—C(1)′	112 (1)
C(3)—C(4)—O(8)	108 (2)	O(9)—C(1)′—C(2)′	110 (2)
C(4)—O(8)—C(5)	108 (1)		
18-Crown-6 (ring centered at 0,0,0)			
C(7)—C(8)	1·41 (4)	O(11)—C(11)	1·48 (2)
C(8)—O(10)	1·35 (3)	C(11)—C(12)	1·47 (3)
O(10)—C(9)	1·45 (3)	C(12)—O(12)	1·40 (3)
C(9)—C(10)	1·52 (3)	O(12)—C(7)′	1·36 (3)
C(10)—O(11)	1·40 (3)		
C(7)—C(8)—O(10)	125 (2)	O(11)—C(11)—C(12)	108 (2)
C(8)—O(10)—C(9)	123 (2)	C(11)—C(12)—O(12)	114 (2)
O(10)—C(9)—C(10)	104 (2)	C(12)—O(12)—C(7)′	96 (2)
C(9)—C(10)—O(11)	108 (2)	O(12)—C(7)′—C(8)′	114 (2)
C(10)—O(11)—C(11)	111 (1)		

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34730 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Comparison of selected bond distances* (Å) *and angles* (°) (*and their means*)

	C–C	C–O	C–O–C	O–C–C
18-Crown-6 (Dunitz & Seiler, 1974)	1·505 (1·507) 1·509	1·403 (1·411) 1·426	113·3 (113·5) 114·0	106·4 (109·8) 114·6
$[Mn(H_2O)_6](ClO_4)_2$. 18-crown-6	1·43 (1·47) 1·50	1·42 (1·44) 1·46	108 (110) 112	106 (108) 110
(This work)	1·41 (1·47) 1·52	1·35 (1·41) 1·48	96 (110) 123	104 (112) 125
$[Co(H_2O)_6][CoCl_4]$. 18-crown-6.acetone	1·48 (1·49) 1·50	1·41 (1·43) 1·44	112·5 (112·9) 113·1	107·6 (110·4) 113·4
(Vance, Holt, Pierpont & Holt, 1980)	1·36 (1·45) 1·54	1·36 (1·43) 1·49	116·1 (116·9) 118·0	108·5 (111·2) 115·7
$[U(H_2O)_2(NO_3)_2O_2].2H_2O$. 18-crown-6 (Eller & Penneman, 1976)	1·48 (1·49) 1·50	1·42 (1·43) 1·45	110·4 (111·0) 112·0	108·0 (108·7) 109·5
$[U(H_2O)_2(NO_3)_2O_2]$. 18-crown-6 (Bombieri, de Paoli & Immirzi, 1978*b*)	1·44 (1·48) 1·54	1·42 (1·48) 1·59	105 (111) 117	101 (108) 113
$[UCl_3(18\text{-crown-}6)]_2[UCl_3(H_2O)$-	1·23 (1·33) 1·43	1·37 (1·47) 1·58	115 (121) 129	102 (112) 125
$O_2(OH)].CH_3NO_2$ (Bombieri, de Paoli & Immirzi, 1978*a*)	1·27 (1·48) 1·61	1·29 (1·46) 1·63	104 (109) 114	100 (107) 116

Table 4. *Possible hydrogen-bonded contacts* (Å)

O(1)–O(7)	2·84 (1)	O(1)–O(8)	2·87 (1)
O(2)–O(13)	2·90 (1)	O(2)–O(17)	2·86 (2)
O(3)–O(11)	2·84 (1)	O(3)–O(16)	2·87 (1)
O(4)–O(10)	2·80 (1)	O(4)–O(12)	2·91 (2)
O(5)–O(9)	2·84 (1)	O(5)–O(19)	2·96 (2)
O(6)–O(14)	3·11 (1)	O(6)–O(18)	2·84 (2)

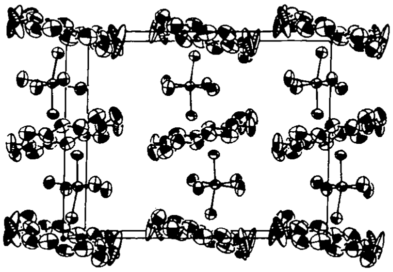

Fig. 2. View of the packing of $[Mn(H_2O)_6]$ and 18-crown-6 in the unit cell.

The polyether rings show average angles and distances comparable to those observed in other 18-crown-6 structures (Table 3), except for those involving C(7) and C(8) (Table 2). Temperature factors for these atoms are highly anisotropic suggesting partial-occupancy positions close to the reported sites. Such positions were calculated but failed to refine.

It has been suggested (Goldberg, 1978) that conformational disorder may occur in crown ether structures when a ring oxygen fails to have hydrogen-bonded contacts. The title structure shows at least one O(polyether)–O(water) contact distance (≤ 2·86 Å) per ring oxygen (Table 4). Disorder was also observed in $[Co(H_2O)_6][CoCl_4]$. 18-crown-6. acetone (Vance, Holt, Pierpont & Holt, 1980; Vance, 1978) and in $[UCl_3(18\text{-crown-}6)]_2[UCl_3(H_2O)O_2(OH)].CH_3NO_2$ (Bombieri, de Paoli & Immirzi, 1978*a*).

A chain of canted polyether rings extends along the *a* axis of the cell with the cations situated off-center from the chain axis (Fig. 2).

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