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Complexes of Manganese and Zinc Di-*tert*-butylnaphthalenesulfonate with Cyclohexano-15-crown-5 Ether Toluene Solvate

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Abstract. (1) Bis(3,7-di-*tert*-butylnaphthalenesulfonato)(2,5,8,11,14-pentaoxabicyclo[13.4.0]nonadecane)manganese monohydrate toluene (1/1), $Mn(C_{18}H_{23}O_3S)_2(C_{14}H_{26}O_5).H_2O.C_7H_8$, $M_r = 1078{\cdot}33$, monoclinic, $P2_1/c$, $a = 12{\cdot}737\ (1)$, $b = 39{\cdot}460\ (4)$, $c = 12{\cdot}765\ (1)$ Å, $\beta = 116{\cdot}40\ (1)^\circ$, $V = 5747\ (2)$ Å^3, $Z = 4$, $D_m = 1{\cdot}24$, $D_x = 1{\cdot}25$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 3{\cdot}47$ cm^{-1}, $F(000) = 2308$, $T = 297$ K, $R(F) = 0{\cdot}069$ for 3060 reflections $[I > 2\sigma(I)]$. (2) Bis(3,7-di-*tert*-butylnaphthalenesulfonato)(2,5,8,11,14-pentaoxabicyclo[13.4.0]nonadecane)zinc monohydrate toluene (1/1), $Zn(C_{18}H_{23}O_3S)_2(C_{14}H_{26}O_5).H_2O.C_7H_8$, $M_r = 1088{\cdot}77$, monoclinic, $P2_1/c$, $a = 12{\cdot}766\ (2)$, $b = 39{\cdot}083\ (5)$, $c = 12{\cdot}771\ (2)$ Å, $\beta = 116{\cdot}44\ (1)^\circ$, $V = 5705\ (2)$ Å^3, $Z = 4$, $D_m = 1{\cdot}28$, $D_x = 1{\cdot}27$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 5{\cdot}69$ cm^{-1}, $F(000) = 2328$, $T = 297$ K, $R(F) = 0{\cdot}067$ for 2240 reflections $[I > 2\sigma(I)]$. Complexes are isostructural. The cation is inside the crown and bonded to its five O atoms and to one O atom of a sulfonate and to one water molecule, forming a pentagonal bipyramid coordination. The second sulfonate ion is hydrogen bonded to the water. There is disorder affecting a *tert*-butyl group and possibly the toluene solvate.

Introduction. The ligands used in this work, cyclohexano-15-crown-5 (CH15C5) and di-*tert*-butylnaphthalenesulfonic acid (HDtBNS) are models for the more extensively alkylated ligands used in solvent extraction studies, *tert*-butylcyclohexano-15-crown-5 and didodecylnaphthalenesulfonic acid. When a mixture of the latter two compounds was used to extract the divalent transition metals Mn, Fe, Co, Ni, Cu and Zn, macrocycle-induced enhancement in the extraction by the sulfonic acid occurred only for Mn and Zn (McDowell, Moyer, Case & Case, 1986; Lumetta, Moyer & Johnson, 1990). The fact that these d^5 and d^{10} ions behave differently suggests that ligand-field effects may be important here; thus a structure determination is needed to ascertain the distribution of O atoms about the cation. Specifically, octahedral or pentagonal bipyramidal coordination would be expected, depending on whether the cation resides within the macro-ring and on whether the sulfonate ions are directly attached to it. IR spectral studies of the extraction system above indicate that the crown ether and water compete in forming inner-sphere complexes with these ions (Lumetta & Moyer, 1991).

No previous structures of Mn^{2+} complexed by 15-crown-5 are known, and those with 18-crown-6 do not have the Mn^{2+} ion attached to the ring (Knöchel, Kopf, Oehler & Rudolph, 1978). Several zinc chloride complexes have been crystallized with the Zn atom in the 15-crown-5 cavity, including $[ZnCl(15\text{-crown-}5)H_2O]_2Zn_2Cl_6$ (Ivakina, Bel'sky, Strel'tsova, Storozhenko & Bulychev, 1989), $[ZnCl(15\text{-crown-}5)(C_3H_6O_2)]_2Zn_2Cl_6$ and $[Zn(15\text{-crown-}5)(CH_3CN)_2]Zn_2Cl_6(CH_3CN)$ (Bel'sky, Strel'tsova, Bulychev, Storozhenko, Ivakina & Gorbunov, 1989). Yet in $ZnCl_2(H_2O)_2(15\text{-crown-}5)$ the Zn atom is not bonded to the crown (Dejehet, Debuyst & Declercq, 1986). No structures involving CH15C5 are yet reported.

Experimental.

Synthesis of (1). 3,7-Di-*tert*-butylnaphthalenesulfonic acid (HDtBNS) was prepared using a published

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procedure (Garbutt, Pachler & Parrish, 1965). HDtBNS (0·532 g, 1·66 mmol) and $MnCO_3$ (0·625 g, 5·44 mmol) in 50 ml of 95% ethanol, refluxed 1 h, filtered hot. The filtrate was evaporated and the $Mn(DtBNS)_2$ redissolved in boiling ethanol–water (1/1), then partially evaporated to yield a white precipitate which was filtered off and air dried. This $Mn(DtBNS)_2$ (0·296 g) was mixed with cyclohexano-15-crown-5 (CH15C5) (0·101 g) in refluxing CCl_4. Solution was filtered hot and filtrate evaporated to yield a white powder. Redissolved in toluene and this solvent removed slowly by vapor diffusion into dodecane over P_2O_5 to yield colorless crystals of $Mn(DtBNS)_2(CH15C5).H_2O$.toluene, (1).

Synthesis of (2). An aqueous solution of HDtBNS (0·234 g), $Ba(OH)_2.H_2O$ (0·120 g) and $ZnSO_4.7H_2O$ (0·107 g) was heated to boiling, filtered hot and the filtrate evaporated to yield $Zn(DtBNS)_2$. This was dissolved in a toluene solution of CH15C5 (0·100 g). Slow evaporation as with (1) yielded colorless crystals of $Zn(DtBNS)_2(CH15C5).H_2O$.toluene, (2).

Crystal data and structure determination. Many of the crystal data and experimental details are presented in the *Abstract* and in Table 1. Colorless thick plates of (1) and (2) were sealed in thin-walled glass tubes to impede loss of toluene and studied by precession methods before mounting on the diffractometer where intensities were measured. Fewer data for (2) were obtained because the crystal was smaller. All the data were corrected with Lorentz and polarization factors, calculated absorption factors based on crystal shape, and for variation of three reference reflections in each case. All calculations employed *Enraf–Nonius Structure Determination Package* (Frenz, 1983). *MULTAN*82 and Fourier syntheses were used to determine the structure of (1), and (2) was found to be isostructural. All atoms are in general positions of $P2_1/c$. One *tert*-butyl group is disordered, and its three methyl C atoms appear in the Fourier map as a number of overlapping peaks. Hence the three methyl C atoms were represented by a distribution over seven sites corresponding to peaks. This is not a unique description, but a more detailed model is not warranted from the data or the chemical significance of this group. H atoms are included in calculated, fixed positions, except none are added for methyl groups or the toluene molecule.

Full-matrix least-squares refinements of the structures, based on F, included anisotropic thermal parameters on all non-H atoms except the disordered ones, for which isotropic values were used. Occupancies for these were adjusted to make the thermal parameters approximately equal. H-atom B values were set equal to the B_{eq} of the atoms to which they are attached. Observations were weighted as $w = 4F_o^2/\{[\sigma(I)]^2 + (0{\cdot}05F_o^2)^2\}$, where I = scaled, observed intensity. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV) and anomalous dispersion from Cromer & Liberman (1970). Final Δ/σ values were $\leqslant 1{\cdot}0$ except for C(30*F*) in (1) and C(50) in (2) which were 1·4 and 1·3, respectively. These atomic sites involve disorder. Final difference Fourier syntheses showed $\rho_{max} = 0{\cdot}37$, $\rho_{min} = -0{\cdot}29$ e Å^{-3} in (1) and $\rho_{max} = 0{\cdot}44$, $\rho_{min} = -0{\cdot}26$ e Å^{-3} in (2); the maxima were in the vicinity of disordered butyl groups. Atomic coordinates and equivalent isotropic thermal parameters are given in Tables 2 and 3.[*] The principal bond lengths are listed in Table 4.

Table 1. *Crystal data and experimental details*

	(1)	(2)
Crystal dimensions (mm)	0·17 × 0·18 × 0·14	0·08 × 0·28 × 0·22
Density by flotation (g cm^{-3})	1·24	1·28
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Scan type	ω–2θ	ω–2θ
Cell parameters		
Number of reflections	25	15
2θ range (°)	14–23	9–20
Transmission factors	0·894–0·968	0·892–0·956
Max. sinθ/λ (Å^{-1})	0·482	0·482
h, *k*, *l* range	0–12; 0–32; −11–10	0–11; 0–32; −11–10
Reference reflections and variation (%)	$6,\overline{11},3$, $3,17,\bar{1}$, $3\bar{1}3$ −10·3, −8·3, −8·3	$27\bar{2}$, $\bar{2}71$, $\bar{1}81$ −5·2, −10·5, −10·5
Number reflections measured	6419	4395
Number unique reflections	4259	2470
R_{int}	0·03	0·02
Number unobserved reflections [$I < 2\sigma(I)$]	1100	230
Number reflections used in refinement	3060	2240
Number parameters refined	650	650
R	0·069	0·067
wR	0·092	0·077
S	2·64	2·26

Discussion. An asymmetric unit of the structure of (1) is shown in Fig. 1. The structure of (2) is so similar as not to warrant a separate figure. The Mn^{2+} and Zn^{2+} ions are bonded to O atoms arranged in a pentagonal bipyramid: five from the crown ether, one from a naphthalene sulfonate molecule and one from a water molecule. Each cation is 0·07 Å from the best plane through the ether O atoms, which themselves deviate from it by up to ±0·13 Å. The average Zn—O (ether) distance, 2·213 Å, is only 0·03 Å less than the average Mn—O (ether) distance, although the respective apical *M*—O distances differ by 0·10 Å. This suggests that the Mn atom provides a slightly better fit to the cavity of the ether, although both are well accommodated as is reflected in the torsion angles of the ring (Table 5). In macrocyclic ethers torsion angles about C—C bonds are usually ~60 and about C—O bonds ~180°. The largest deviations from these values in

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[*] Tables of structure factors, anisotropic thermal parameters, H-atom parameters, least-squares planes and selected angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54114 (50 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional atomic coordinates and the equivalent isotropic thermal parameters for* $Mn(DtBNS)_2.CH$-15-*crown*-5

$$B_{eq} = (4/3)\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Mn	0·6777 (1)	0·09322 (4)	0·0149 (1)	4·31 (4)
S(1)	0·6913 (2)	−0·03421 (7)	−0·0462 (2)	4·95 (7)
S(2)	0·7328 (2)	0·16263 (6)	−0·1102 (2)	3·93 (6)
O(1)	0·5136 (6)	0·1124 (2)	0·0158 (5)	6·5 (2)
O(2)	0·5264 (5)	0·0878 (2)	−0·1689 (5)	6·0 (2)
O(3)	0·7462 (6)	0·0649 (2)	−0·0837 (6)	7·9 (2)
O(4)	0·8669 (6)	0·0783 (2)	0·1295 (6)	7·0 (2)
O(5)	0·7214 (6)	0·1154 (2)	0·1938 (5)	6·5 (2)
O(6)	0·7137 (6)	−0·0152 (2)	0·0590 (5)	6·8 (2)
O(7)	0·7259 (6)	−0·0171 (2)	−0·1248 (5)	6·8 (2)
O(8)	0·5718 (5)	−0·0468 (2)	−0·1047 (5)	5·9 (2)
O(9)	0·7366 (6)	0·1401 (2)	−0·0156 (5)	4·8 (2)
O(10)	0·6688 (5)	0·1476 (2)	−0·2241 (5)	5·7 (2)
O(11)	0·8485 (4)	0·1743 (2)	−0·0858 (5)	5·0 (2)
O(12)	0·6238 (5)	0·0467 (2)	0·0672 (5)	5·3 (2)
C(1)	0·4173 (8)	0·1187 (3)	−0·0953 (9)	7·8 (4)
C(2)	0·4156 (9)	0·0899 (4)	−0·171 (1)	8·2 (4)
C(3)	0·552 (1)	0·0580 (3)	−0·223 (1)	11·1 (5)
C(4)	0·673 (1)	0·0601 (4)	−0·204 (1)	11·5 (4)
C(5)	0·868 (1)	0·0568 (3)	−0·041 (1)	9·4 (4)
C(6)	0·927 (1)	0·0778 (4)	0·060 (1)	9·7 (4)
C(7)	0·9144 (9)	0·1002 (4)	0·231 (1)	9·2 (4)
C(8)	0·827 (1)	0·1010 (3)	0·277 (1)	9·4 (5)
C(9)	0·6208 (9)	0·1140 (4)	0·2192 (8)	8·4 (4)
C(10)	0·647 (1)	0·1330 (4)	0·335 (1)	11·7 (5)
C(11)	0·677 (1)	0·1708 (5)	0·327 (1)	14·2 (6)
C(12)	0·572 (1)	0·1857 (4)	0·223 (1)	13·4 (6)
C(13)	0·544 (1)	0·1661 (4)	0·107 (1)	11·7 (5)
C(14)	0·524 (1)	0·1308 (3)	0·1130 (9)	7·5 (4)
C(15)	0·7803 (7)	−0·0712 (2)	0·0021 (7)	3·5 (2)
C(16)	0·7798 (6)	−0·0960 (2)	−0·0796 (6)	3·2 (2)
C(17)	0·7132 (6)	−0·0936 (2)	−0·2022 (6)	3·5 (2)
C(18)	0·7187 (7)	−0·1176 (3)	−0·2768 (7)	4·6 (3)
C(19)	0·7936 (8)	−0·1460 (3)	−0·2270 (8)	5·6 (3)
C(20)	0·8572 (8)	−0·1492 (3)	−0·1106 (8)	5·2 (3)
C(21)	0·8529 (7)	−0·1242 (2)	−0·0329 (7)	4·0 (3)
C(22)	0·9246 (7)	−0·1280 (2)	0·0899 (7)	4·4 (3)
C(23)	0·9241 (7)	−0·1041 (2)	0·1672 (7)	4·3 (3)
C(24)	0·8499 (7)	−0·0758 (2)	0·1204 (7)	4·2 (3)
C(25)	0·6467 (8)	−0·1150 (3)	−0·4116 (7)	6·1 (3)
C(26)	0·737 (1)	−0·1105 (4)	−0·4618 (9)	9·9 (4)
C(27)	0·560 (1)	−0·0851 (3)	−0·4487 (9)	7·5 (4)
C(28)	0·578 (1)	−0·1501 (3)	−0·457 (1)	8·7 (4)
C(29)	0·9993 (8)	−0·1074 (3)	0·3015 (8)	5·8 (3)
C(30*A*)	1·065 (1)	−0·1423 (5)	0·337 (1)	7·6 (5)*
C(30*B*)	1·130 (3)	−0·093 (1)	0·330 (3)	4·8 (9)*
C(30*C*)	1·076 (1)	−0·0757 (5)	0·351 (1)	7·4 (5)*
C(30*D*)	0·979 (3)	−0·076 (1)	0·365 (3)	6 (1)*
C(30*E*)	0·953 (4)	−0·134 (1)	0·348 (4)	8 (1)*
C(30*F*)	1·133 (4)	−0·125 (1)	0·327 (4)	4 (1)*
C(30*G*)	0·914 (1)	−0·1059 (5)	0·360 (1)	7·6 (4)*
C(31)	0·6513 (6)	0·1983 (2)	−0·1054 (6)	3·1 (2)
C(32)	0·6930 (6)	0·2205 (2)	−0·0079 (6)	2·7 (2)
C(33)	0·7999 (6)	0·2167 (2)	0·0953 (7)	3·3 (2)
C(34)	0·8348 (6)	0·2393 (2)	0·1884 (7)	3·6 (2)
C(35)	0·7655 (7)	0·2675 (3)	0·1785 (7)	4·4 (3)
C(36)	0·6608 (7)	0·2717 (2)	0·0815 (7)	4·6 (3)
C(37)	0·6180 (7)	0·2488 (2)	−0·0153 (7)	3·8 (2)
C(38)	0·5046 (7)	0·2520 (3)	−0·1124 (7)	4·0 (3)
C(39)	0·4636 (7)	0·2297 (2)	−0·2026 (7)	3·8 (2)
C(40)	0·5416 (7)	0·2028 (2)	−0·1981 (7)	3·9 (3)
C(41)	0·9488 (7)	0·2358 (3)	0·3004 (8)	5·2 (3)
C(42)	1·0186 (9)	0·2044 (3)	0·2949 (9)	7·9 (4)
C(43)	0·9225 (9)	0·2347 (4)	0·4069 (8)	8·0 (4)
C(44)	1·024 (1)	0·2685 (3)	0·311 (1)	8·8 (4)
C(45)	0·3425 (7)	0·2319 (3)	−0·3073 (7)	5·2 (3)
C(46)	0·3557 (9)	0·2357 (3)	−0·4202 (7)	7·1 (4)
C(47)	0·2740 (8)	0·2622 (3)	−0·2959 (9)	7·1 (3)
C(48)	0·2748 (9)	0·1982 (3)	−0·313 (1)	7·9 (4)
C(49)	0·116 (2)	0·0160 (5)	0·302 (2)	18·7 (9)
C(50)	0·190 (1)	0·0087 (4)	0·424 (2)	14·7 (8)
C(51)	0·281 (1)	−0·0024 (4)	0·453 (2)	14·4 (7)
C(52)	0·369 (2)	−0·0143 (5)	0·560 (4)	36 (2)
C(53)	0·342 (2)	−0·0094 (6)	0·642 (2)	25 (1)
C(54)	0·236 (2)	0·0034 (6)	0·634 (2)	22 (1)
C(55)	0·154 (2)	0·0126 (4)	0·514 (1)	21·2 (6)

* Isotropic temperature factors. Occupancy factors, beginning with C(30*A*): 0·7, 0·25, 0·65, 0·25, 0·25, 0·2 and 0·7.

Table 3. *Fractional atomic coordinates and the equivalent isotropic thermal parameters for* $Zn(DtBNS)_2.CH$-15-*crown*-5

$$B_{eq} = (4/3)\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Zn	0·6765 (1)	0·09386 (4)	0·0180 (1)	3·53 (4)
S(1)	0·6834 (3)	−0·0337 (1)	−0·0494 (3)	4·1 (1)
S(2)	0·7331 (3)	0·1616 (1)	−0·1009 (3)	3·3 (1)
O(1)	0·5180 (8)	0·1126 (2)	0·0225 (7)	5·0 (3)
O(2)	0·5235 (8)	0·0899 (2)	−0·1632 (7)	4·9 (3)
O(3)	0·7390 (8)	0·0670 (3)	−0·0851 (8)	6·1 (3)
O(4)	0·8644 (8)	0·0786 (3)	0·1318 (8)	5·1 (3)
O(5)	0·7284 (7)	0·1148 (3)	0·1990 (8)	5·2 (3)
O(6)	0·7088 (9)	−0·0137 (2)	0·0556 (8)	6·1 (3)
O(7)	0·7160 (8)	−0·0167 (3)	−0·1302 (8)	6·0 (3)
O(8)	0·5632 (7)	−0·0471 (2)	−0·1044 (8)	4·6 (3)
O(9)	0·7333 (7)	0·1395 (2)	−0·0041 (7)	4·0 (3)
O(10)	0·6709 (8)	0·1472 (2)	−0·2169 (7)	4·6 (3)
O(11)	0·8514 (7)	0·1731 (2)	−0·0722 (7)	3·9 (3)
O(12)	0·6284 (7)	0·0484 (2)	0·0669 (7)	4·0 (3)
C(1)	0·422 (1)	0·1199 (4)	−0·086 (1)	4·7 (5)
C(2)	0·413 (1)	0·0913 (5)	−0·161 (1)	6·1 (5)
C(3)	0·546 (1)	0·0601 (5)	−0·215 (1)	7·3 (6)
C(4)	0·665 (1)	0·0607 (4)	−0·208 (1)	7·2 (6)
C(5)	0·859 (1)	0·0586 (4)	−0·040 (1)	7·3 (6)
C(6)	0·923 (1)	0·0795 (4)	0·063 (1)	6·8 (6)
C(7)	0·918 (1)	0·0998 (5)	0·234 (1)	6·6 (5)
C(8)	0·835 (1)	0·1004 (4)	0·284 (1)	6·8 (6)
C(9)	0·629 (1)	0·1139 (5)	0·225 (1)	6·5 (6)
C(10)	0·655 (2)	0·1315 (5)	0·344 (2)	9·9 (7)
C(11)	0·678 (2)	0·1705 (5)	0·337 (2)	9·6 (7)
C(12)	0·575 (2)	0·1854 (5)	0·229 (2)	10·5 (7)
C(13)	0·550 (1)	0·1674 (5)	0·114 (1)	7·7 (6)
C(14)	0·530 (1)	0·1303 (4)	0·118 (1)	4·8 (5)
C(15)	0·774 (1)	−0·0707 (3)	0·000 (1)	3·0 (4)
C(16)	0·7758 (9)	−0·0959 (3)	−0·081 (1)	2·5 (3)
C(17)	0·709 (1)	−0·0928 (4)	−0·207 (1)	3·2 (4)
C(18)	0·714 (1)	−0·1172 (4)	−0·282 (1)	3·4 (4)
C(19)	0·792 (1)	−0·1449 (4)	−0·232 (1)	4·8 (5)
C(20)	0·858 (1)	−0·1489 (4)	−0·113 (1)	4·2 (4)
C(21)	0·851 (1)	−0·1234 (3)	−0·035 (1)	3·4 (4)
C(22)	0·922 (1)	−0·1268 (3)	0·087 (1)	3·8 (4)
C(23)	0·9193 (9)	−0·1031 (3)	0·165 (1)	3·4 (4)
C(24)	0·844 (1)	−0·0748 (3)	0·118 (1)	3·1 (4)
C(25)	0·644 (1)	−0·1153 (4)	−0·419 (1)	5·0 (5)
C(26)	0·736 (1)	−0·1110 (5)	−0·468 (1)	7·0 (5)
C(27)	0·555 (1)	−0·0852 (4)	−0·454 (1)	5·7 (5)
C(28)	0·573 (1)	−0·1497 (4)	−0·466 (1)	6·6 (6)
C(29)	1·001 (1)	−0·1066 (4)	0·302 (1)	5·2 (5)
C(30*A*)	1·126 (3)	−0·087 (1)	0·336 (4)	4 (1)*
C(30*B*)	0·981 (4)	−0·138 (1)	0·339 (4)	6 (2)*
C(30*C*)	1·070 (2)	−0·0720 (7)	0·347 (2)	4·3 (7)*
C(30*D*)	0·965 (5)	−0·078 (2)	0·367 (5)	3 (2)*
C(30*E*)	1·073 (2)	−0·1434 (7)	0·335 (2)	5·1 (7)*
C(30*F*)	1·124 (4)	−0·124 (1)	0·314 (4)	5 (1)*
C(30*G*)	0·913 (2)	−0·1080 (6)	0·356 (2)	6·1 (6)*
C(31)	0·651 (1)	0·1977 (3)	−0·098 (1)	2·7 (4)
C(32)	0·6937 (9)	0·2206 (3)	0·002 (1)	2·6 (4)
C(33)	0·802 (1)	0·2165 (3)	0·102 (1)	2·8 (4)
C(34)	0·838 (1)	0·2398 (3)	0·196 (1)	3·3 (4)
C(35)	0·765 (1)	0·2683 (4)	0·184 (1)	4·0 (5)
C(36)	0·659 (1)	0·2733 (4)	0·091 (1)	3·3 (4)
C(37)	0·620 (1)	0·2491 (3)	−0·004 (1)	3·2 (4)
C(38)	0·503 (1)	0·2526 (4)	−0·104 (1)	3·4 (4)
C(39)	0·463 (1)	0·2303 (4)	−0·196 (1)	3·4 (4)
C(40)	0·540 (1)	0·2018 (4)	−0·193 (1)	3·2 (4)
C(41)	0·955 (1)	0·2370 (4)	0·308 (1)	3·8 (4)
C(42)	1·025 (1)	0·2041 (4)	0·305 (1)	6·2 (5)
C(43)	0·927 (1)	0·2351 (5)	0·415 (1)	6·3 (5)
C(44)	1·029 (1)	0·2696 (4)	0·315 (1)	6·7 (6)
C(45)	0·343 (1)	0·2323 (4)	−0·302 (1)	3·9 (4)
C(46)	0·358 (1)	0·2353 (4)	−0·414 (1)	5·6 (5)
C(47)	0·277 (1)	0·2630 (4)	−0·284 (1)	6·0 (5)
C(48)	0·278 (1)	0·1984 (4)	−0·305 (1)	7·0 (6)
C(49)	0·099 (3)	0·0202 (7)	0·295 (2)	19 (1)
C(50)	0·173 (2)	0·0097 (6)	0·414 (4)	28 (2)
C(51)	0·266 (3)	−0·0003 (6)	0·434 (2)	18 (1)
C(52)	0·336 (2)	−0·0092 (6)	0·521 (2)	19 (1)
C(53)	0·352 (2)	−0·0125 (6)	0·644 (3)	27 (2)
C(54)	0·252 (3)	−0·0008 (6)	0·637 (2)	22 (1)
C(55)	0·155 (2)	0·0126 (5)	0·525 (2)	17·8 (8)

* Isotropic temperature factors. Occupancy factors, beginning with C(30*A*): 0·3, 0·3, 0·55, 0·2, 0·6, 0·3 and 0·75.

Table 4. *Selected bond lengths* (Å)

	M = Mn	*M* = Zn		*M* = Mn	*M* = Zn
M—O(1)	2·228 (5)	2·177 (9)	C(25)—C(27)	1·54 (1)	1·56 (2)
M—O(2)	2·290 (5)	2·274 (8)	C(10)—C(9)	1·56 (1)	1·56 (2)
M—O(3)	2·138 (6)	2·099 (9)	C(11)—C(10)	1·55 (2)	1·56 (2)
M—O(4)	2·271 (5)	2·262 (9)	C(12)—C(11)	1·52 (2)	1·53 (2)
M—O(5)	2·272 (5)	2·256 (9)	C(13)—C(12)	1·56 (2)	1·53 (2)
M—O(9)	2·097 (4)	1·992 (8)	C(14)—C(13)	1·42 (2)	1·48 (2)
M—O(12)	2·167 (4)	2·065 (7)	C(31)—C(32)	1·418 (8)	1·45 (1)
S(1)—O(6)	1·452 (5)	1·458 (8)	C(32)—C(33)	1·420 (7)	1·42 (2)
S(1)—O(7)	1·432 (5)	1·436 (8)	C(33)—C(34)	1·391 (8)	1·40 (2)
S(1)—O(8)	1·453 (5)	1·471 (8)	C(34)—C(35)	1·391 (8)	1·41 (2)
S(1)—C(15)	1·782 (6)	1·78 (1)	C(35)—C(36)	1·368 (8)	1·36 (2)
S(2)—O(9)	1·483 (4)	1·507 (8)	C(36)—C(37)	1·429 (8)	1·44 (2)
S(2)—O(10)	1·441 (4)	1·447 (8)	C(37)—C(32)	1·445 (8)	1·44 (1)
S(2)—O(11)	1·440 (4)	1·457 (7)	C(37)—C(38)	1·431 (8)	1·48 (2)
S(2)—C(31)	1·766 (6)	1·77 (1)	C(38)—C(39)	1·356 (8)	1·37 (2)
C(1)—O(1)	1·425 (9)	1·41 (1)	C(39)—C(40)	1·438 (8)	1·47 (2)
C(2)—C(1)	1·49 (1)	1·44 (2)	C(40)—C(31)	1·383 (7)	1·41 (1)
O(2)—C(2)	1·40 (1)	1·42 (1)	C(49)—C(50)	1·45 (8)	1·45 (8)
C(3)—O(2)	1·47 (1)	1·43 (2)	C(50)—C(51)	1·14 (8)	1·17 (8)
C(4)—C(3)	1·45 (1)	1·48 (2)	C(51)—C(52)	1·41 (8)	1·13 (8)
O(3)—C(4)	1·41 (2)	1·45 (2)	C(52)—C(53)	1·25 (8)	1·50 (8)
C(5)—O(3)	1·43 (1)	1·41 (2)	C(53)—C(54)	1·40 (8)	1·32 (8)
C(6)—C(5)	1·43 (1)	1·45 (2)	C(54)—C(55)	1·47 (6)	1·51 (6)
O(4)—C(6)	1·41 (1)	1·39 (2)	C(55)—C(50)	1·42 (9)	1·54 (9)
C(7)—O(4)	1·45 (1)	1·44 (2)	C(25)—C(28)	1·60 (2)	1·58 (2)
C(8)—C(7)	1·47 (1)	1·46 (2)	C(23)—C(29)	1·553 (9)	1·59 (2)
O(5)—C(8)	1·41 (1)	1·43 (1)	C(29)—C(30*A*)	1·57 (1)	1·64 (4)
C(9)—O(5)	1·46 (1)	1·45 (2)	C(29)—C(30*B*)	1·64 (3)	1·38 (5)
C(14)—C(9)	1·52 (1)	1·53 (2)	C(29)—C(30*C*)	1·54 (2)	1·58 (2)
O(1)—C(14)	1·392 (9)	1·35 (2)	C(29)—C(30*D*)	1·56 (3)	1·58 (6)
C(15)—C(16)	1·428 (8)	1·44 (1)	C(29)—C(30*E*)	1·45 (4)	1·66 (2)
C(16)—C(17)	1·413 (8)	1·45 (1)	C(29)—C(30*F*)	1·73 (4)	1·65 (4)
C(17)—C(18)	1·367 (8)	1·37 (1)	C(29)—C(30*G*)	1·57 (2)	1·56 (2)
C(18)—C(19)	1·425 (9)	1·42 (2)	C(34)—C(41)	1·525 (8)	1·54 (2)
C(19)—C(20)	1·345 (9)	1·38 (2)	C(41)—C(42)	1·55 (1)	1·58 (1)
C(20)—C(21)	1·417 (9)	1·44 (2)	C(41)—C(43)	1·54 (1)	1·56 (2)
C(21)—C(16)	1·403 (8)	1·39 (1)	C(41)—C(44)	1·58 (1)	1·56 (2)
C(21)—C(22)	1·429 (9)	1·42 (2)	C(39)—C(45)	1·529 (8)	1·53 (2)
C(22)—C(23)	1·367 (8)	1·37 (2)	C(45)—C(46)	1·531 (9)	1·53 (2)
C(23)—C(24)	1·413 (9)	1·41 (1)	C(45)—C(47)	1·525 (9)	1·54 (1)
C(24)—C(15)	1·382 (8)	1·38 (1)	C(45)—C(48)	1·57 (1)	1·55 (2)
C(18)—C(25)	1·552 (9)	1·57 (2)	O(12)···O(6)	2·719 (9)	2·664 (9)
C(25)—C(26)	1·56 (1)	1·57 (2)	O(12)···O(8^i)	2·738 (9)	2·694 (9)

Symmetry code: (i) $1 - x, -y, -z$.

Table 5. *Torsion angles* (°)

	Mn	Zn
O(1)—C(1)—C(2)—O(2)	−55 (1)	−58 (2)
C(1)—C(2)—O(2)—C(3)	171 (1)	170 (1)
C(2)—O(2)—C(3)—C(4)	−176 (1)	−177 (1)
O(2)—C(3)—C(4)—O(3)	53 (1)	52 (2)
C(3)—C(4)—O(3)—C(5)	160 (1)	161 (1)
C(4)—O(3)—C(5)—C(6)	154 (1)	156 (1)
O(3)—C(5)—C(6)—O(4)	43 (1)	46 (2)
C(5)—C(6)—O(4)—C(7)	−176 (1)	−177 (1)
C(6)—O(4)—C(7)—C(8)	171 (1)	171 (1)
O(4)—C(7)—C(8)—O(5)	−63 (1)	−61 (2)
C(7)—C(8)—O(5)—C(9)	172 (1)	173 (1)
C(8)—O(5)—C(9)—C(14)	−179 (1)	−179 (1)
O(5)—C(9)—C(14)—O(1)	57 (1)	56 (2)
C(9)—C(14)—O(1)—C(1)	170 (1)	172 (1)
C(14)—O(1)—C(1)—C(2)	−166 (1)	−163 (1)

(1) and (2) are 26 and 24°, respectively, which indicates little strain. Presently no other structures for CH15C5 are reported, but two complexes which are known to have equally good fit of ring and cation are Mg(benzo-15-crown-5)(NCS)$_2$ (Owen, 1978) and Cu(benzo-15-crown-5)Cl$_2$.CHCl$_3$ (Sakurai, Kobayashi, Tsuboyama, Kohno, Azuma & Ishizu, 1983). The ions lie in the ether plane and torsion angles deviate, at a maximum, from expected values by 12 and 18°, respectively (excluding the benzo group). On the other hand, complexes of Zn, mentioned above, with unsubstituted 15-crown-5 exhibit torsion-angle deviations up to 60° from expected values; and complexes of this ether with larger ions show deviations up to 100°. A few examples of these include Ba(15-crown-5)Br$_2$.2H$_2$O (Feneau-Dupont, Arte, Declercq, Germain & Van Meerssche, 1979), Na(15-crown-5)ClO$_4$ (Shoham & Cohen, 1989), and Y(15-crown-5)Cl$_3$.8H$_2$O (Rogers & Kurihara, 1987). All these ligands, including CH15C5, are quite flexible; even the uncomplexed benzo-15-crown-5 has quite large torsion-angle variations (Hanson, 1978). Thus, it is primarily the cation being complexed that establishes the conformation of the ether.

There are other features of note in the structure of (1) and (2). The cyclohexyl groups are in the chair conformation and are *cis* to the coordinated DtBNS

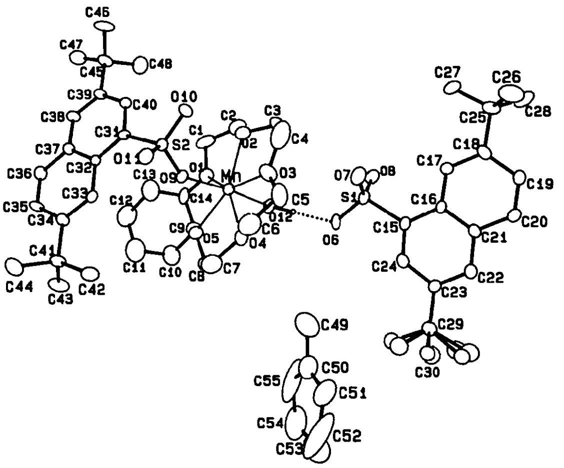

Fig. 1. One asymmetric unit of the structure of Mn(DtBNS)$_2$.CH15C5.H$_2$O.toluene. Atoms represented by 20% probability ellipsoids.

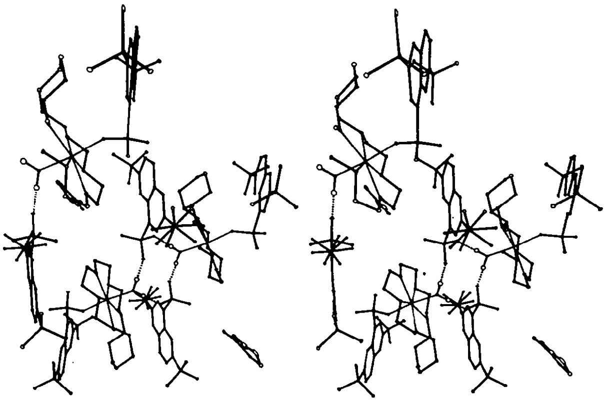

Fig. 2. Stereoscopic drawing of a portion of the structure of (1) to shown hydrogen bonding.

ligands. Only one of the four *tert*-butyl groups is disordered; it is not apparent why this is, but is well established by the electron-density maps. The toluene molecule is held loosely in the lattice and is poorly determined. Crystals left out in the atmosphere lose this solvent quickly and the samples used for study may have lost some before being encapsulated.

In Fig. 2 are shown the intermolecular connections. Hydrogen bonds from the water molecule [O(12)] to naphthalenesulfonate atoms, O(6) and O(8), of two different molecules link the structure into large centrosymmetric dimers. Toluene molecules occupy spaces between them.

In summary, the solution IR studies (Lumetta & Moyer, 1991) are supported by these crystal-structure analyses and the bonding geometry is clarified. The Mn^{2+} and Zn^{2+} ions fit well in the 15-crown-5 ring of CH15C5 where they are bonded to all its O atoms and to an O atom of a sulfonate group and to one water molecule to form a pentagonal bipyramid.

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Structures of Benzenethiolato Complexes of Palladium(II) and Platinum(II)

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Abstract. Bis(tetraphenylphosphonium) di-μ-benzenethiolato-tetrakis(benzenethiolato-$1\kappa^2S,2\kappa^2S$)dipalladate acetonitrile solvate, $[Ph_4P]_2[Pd_2(SPh)_6].2MeCN$ (1), $M_r = 1628·8$, monoclinic, $P2_1/n$, $a = 13·724\ (5)$, $b = 26·306\ (6)$, $c = 10·931\ (4)$ Å, $\beta = 96·71\ (2)°$, $V = 3919·3\ (22)$ Å^3, $Z = 2$, $D_x = 1·38$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 5·9$ cm^{-1}, $F(000) = 1672$, $T = 293$ K, $R = 0·066$ for 2283 observed reflections. $[Pd_2(SPh)_6]^{2-}$ is centrosymmetric and is formed by edge sharing of two square-planar PdS_4 coordinations. Bis(tetraethylammonium) tetra(benzenethiolato)platinate(II), $[Et_4N]_2[Pt(SPh)_4]$ (2), $M_r = 892·4$, monoclinic, $P2_1/n$, $a = 16·419\ (5)$, $b = 12·117\ (2)$, $c = 10·186\ (2)$ Å, $\beta = 91·61\ (2)°$, $V = 2025·7\ (8)$ Å^3, $Z = 2$, $D_x = 1·46$ g cm^{-3}, $\mu = 38·6$ cm^{-1}, λ(Mo $K\alpha$) = 0·71069 Å, $F(000) = 912$, $T = 293$ K, $R = 0·032$ for 2376 observed reflections. $[Pt(SPh)_4]^{2-}$ has a center of symmetry and PtS_4 has square-planar coordination.

Introduction. Some nickel thiolate (Tremel, Kriege, Krebs & Henkel, 1988) and palladium thiolate (Higgins & Suggs, 1988) clusters have been synthesized and structurally characterized by the X-ray diffraction method. In these complexes the coordination geometry around each metal ion is square planar. Reaction of Ni^{2+} with benzenethiolate (SPh^-), however, gives a mononuclear tetrahedral

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