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# Preparation and Crystal Structure of Bis(triethylene glycol-*O*,*O*',*O*'',*O*''')manganese(II) Dibromide

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**Abstract**—A new complex, bis(triethylene glycol-*O*,*O*',*O*'',*O*''')manganese(II) dibromide $[Mn(TEG)_2]^{2+}\cdot 2Br^-$, was prepared. Its structure was studied by single crystal X-ray diffraction. The complex cation $[Mn(TEG)_2]^{2+}$ is of the host–guest type with two TEG ligands (podands) as hosts. Both TEG ligands are disordered and tetradentate, with all the four oxygen atoms of each ligand participating in the coordination. The $Mn^{2+}$ cation has coordination number 8, and its coordination polyhedron is a distorted bisdisphenoid (trigonal dodecahedron). The geometric parameters (bond lengths, bond and torsion angles) of the complex were determined relatively accurately. In the crystal structure, the ions form infinite thick layers by interionic hydrogen bonds O–H···$Br^-$.

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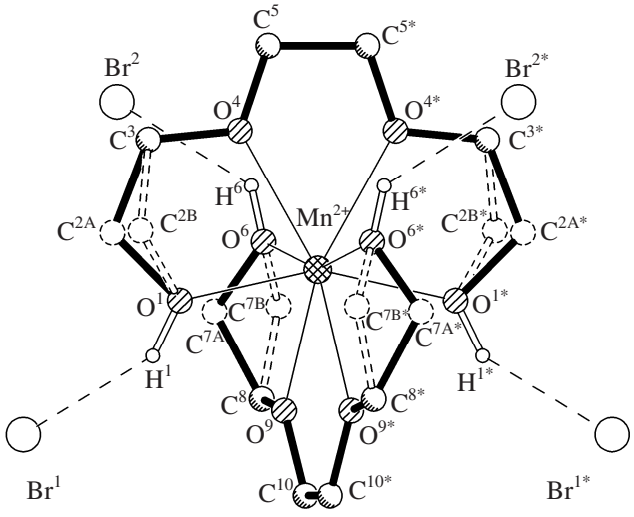
Triethylene glycol $HO(CH_2CH_2O)_3H$ (TEG) exhibits a moderate complexing ability and forms complexes with some metal ions. In the Cambridge Structural Database (version 5.28) [1], there are data on 33 crystal structures of complex compounds containing TEG as a neutral ligand. In most cases, these are complexes of a very narrow range of metals (Y, La, lanthanides, $Ca^{2+}$, $Sr^{2+}$) with one or two TEG ligands.

Here we report on the synthesis and single crystal X-ray diffraction study of a new TEG complex of this type, bis(triethylene glycol-*O*,*O*',*O*'',*O*''')manganese(II) dibromide, $[Mn(TEG)_2]^{2+}\cdot 2Br^-$ (**I**). It is interesting that crystals of **I** appeared to be isomorphous to the crystals of a related complex, bis(triethylene glycol-*O*,*O*',*O*'',*O*''')-strontium dichloride, $[Sr(TEG)_2]^{2+}\cdot 2Cl^-$ (**II**), whose structure was examined previously [2].

The molecular-ionic structure of **I** in the crystal is shown in the figure. The selected bond lengths, bond angles, and torsion angles are given in Tables 1–3. As shown by X-ray diffraction analysis (see Experimental), in the crystal structure of complex **I** two independent $Br^1$ and $Br^2$ anions and the $Mn^{2+}$ cation occupy special positions on different crystallographic axes of symmetry *2*.

As can be seen, in the structure of **I** two TEG ligands in the complex cation $[Mn(TEG)_2]^{2+}$ have the shape of a horseshoe or claw, enveloping the $Mn^{2+}$ cation from two opposite sides. The least-squares planes of their O atoms are almost perpendicular to each other. Both TEG ligands are tetradentate, i.e., all




Molecular-ionic structure of complex **I** in the crystal. The H atoms at the C atoms of the two TEG ligands are omitted for clarity. Crystallographic symmetry axis *2* passes through the center of the $Mn^{2+}$ cation and middles of the $C^5$–$C^{5*}$ and $C^{10}$–$C^{10*}$ bonds. Independent atoms $C^2$ and $C^7$ of the two TEG ligands are disordered each over two positions A and B with occupancies of ~0.5. The atoms symmetrical to the basis atoms relative to axis *2* are marked with asterisks. Single dashed lines denote hydrogen bonds O–H···$Br^-$.

**Table 1.** Selected bond lengths ($d$, Å) in the structure of **I**[a]

| Bond | $d$ | Bond | $d$ |
|---|---|---|---|
| Mn–$O^1$ | 2.223(3) | $O^4$–$C^5$ | 1.369(7) |
| Mn–$O^4$ | 2.398(4) | $C^5$–$C^{5*}$ | 1.474(9) |
| Mn–$O^6$ | 2.217(4) | $O^6$–$C^{7A}$ | 1.44(1) |
| Mn–$O^9$ | 2.426(4) | $O^6$–$C^{7B}$ | 1.40(1) |
| $O^1$–$C^{2A}$ | 1.44(1) | $C^{7A}$–$C^8$ | 1.47(1) |
| $O^1$–$C^{2B}$ | 1.40(1) | $C^{7B}$–$C^8$ | 1.47(1) |
| $C^{2A}$–$C^3$ | 1.47(1) | $C^8$–$O^9$ | 1.400(8) |
| $C^{2B}$–$C^3$ | 1.48(1) | $O^9$–$C^{10}$ | 1.356(7) |
| $C^3$–$O^4$ | 1.386(7) | $C^{10}$–$C^{10*}$ | 1.468(9) |

[a] Atoms symmetrical to the basis atoms (symmetry code: $-x$, $y$, $1/2 - z$) are marked with an asterisk. The same for Tables 2 and 3. See also note a to Table 4.

**Table 2.** Bond angles (ω, deg) in the structure of **I**

| Angle | ω | Angle | ω |
|---|---|---|---|
| $O^1MnO^4$ | 69.6(1) | $MnO^6C^{7A}$ | 120.7(5) |
| $O^1MnO^6$ | 93.3(2) | $MnO^6C^{7B}$ | 118.9(8) |
| $O^1MnO^9$ | 80.0(2) | $MnO^9C^8$ | 114.6(4) |
| $O^1MnO^{1*}$ | 156.5(2) | $MnO^9C^{10}$ | 123.6(4) |
| $O^1MnO^{4*}$ | 133.9(1) | $O^1C^{2A}C^3$ | 111.0(9) |
| $O^1MnO^{6*}$ | 91.0(2) | $O^1C^{2B}C^3$ | 112.3(8) |
| $O^1MnO^{9*}$ | 80.0(2) | $C^{2A}C^3O^4$ | 118.0(7) |
| $O^4MnO^6$ | 84.3(2) | $C^{2B}C^3O^4$ | 105.9(7) |
| $O^4MnO^9$ | 137.9(2) | $C^3O^4C^5$ | 117.3(4) |
| $O^4MnO^{4*}$ | 64.5(2) | $O^4C^5C^{5*}$ | 111.3(4) |
| $O^4MnO^{6*}$ | 77.8(2) | $O^6C^{7A}C^8$ | 107.8(7) |
| $O^4MnO^{9*}$ | 133.9(2) | $O^6C^{7B}C^8$ | 110.0(9) |
| $O^6MnO^9$ | 68.7(2) | $C^{7A}C^8O^9$ | 111.3(7) |
| $O^6MnO^{6*}$ | 158.8(2) | $C^{7B}C^8O^9$ | 114.1(8) |
| $O^6MnO^{9*}$ | 132.5(2) | $C^8O^9C^{10}$ | 120.0(5) |
| $O^9MnO^{9*}$ | 63.8(2) | $O^9C^{10}C^{10*}$ | 113.2(3) |
| $MnO^1C^{2A}$ | 124.5(6) | $H^1O^1C^{2A}$ | 108 |
| $MnO^1C^{2B}$ | 115.2(5) | $H^1O^1C^{2B}$ | 118 |
| $MnO^4C^3$ | 116.0(3) | $H^6O^6C^{7A}$ | 111 |
| $MnO^4C^5$ | 122.5(3) | $H^6O^6C^{7B}$ | 112 |

the four oxygen atoms of each ligand are coordinated with $Mn^{2+}$.

In the structure of **I**, the complex cation $[Mn(TEG)_2]^{2+}$ belongs to the host–guest type [3] with two TEG ligands (podands) as hosts. It has an intrinsic twofold axis coinciding with crystallographic axis *2* and passing along *y*-axis through the center of the $Mn^{2+}$ cation and middles of two bonds $C^5$–$C^{5*}$ and $C^{10}$–$C^{10*}$ of two disordered TEG ligands (therefore, in these ligands only their halves are symmetry-independent).

In the structure of **I**, the coordination number (CN) of the $Mn^{2+}$ cation in the $[Mn(TEG)_2]^{2+}$ ion is 8, and its coordination polyhedron is a distorted bisdisphenoid (trigonal dodecahedron, relatively rare configuration). Its four vertices $O^1$, $O^{1*}$, $O^6$, and $O^{6*}$ are common for five edges each, and the other four vertices $O^4$, $O^{4*}$, $O^9$, and $O^{9*}$ are common for four edges each.

In the $[Mn(TEG)_2]^{2+}$ cation in **I** the mean length of eight coordination bonds Mn–O is 2.316±0.096 Å, with the four Mn–O bonds with the terminal $O^1$ and $O^6$ atoms (2.220±0.003 Å) being appreciably (by ~0.2 Å on the average) shorter than the other four Mn–O bonds with the $O^4$ and $O^9$ atoms (2.412±0.014 Å) of the two TEG ligands. These mean lengths of the Mn–O bonds are close to, or somewhat smaller than the sum of the effective ionic radius of the $Mn^{2+}$ cation (0.96 Å for CN 8) [4] and the van der Waals radius of the oxygen atom (1.40–1.52 Å) [5, 6].

In the crystal structure of **I**, the independent atoms $C^2$ and $C^7$ of the two TEG ligands are disordered each over two approximately equiprobable positions $C^{2A}$, $C^{2B}$ and $C^{7A}$, $C^{7B}$ with occupancies of ~0.5. The distances between these positions are as follows: $C^{2A}\cdots C^{2B}$ 0.60(2) and $C^{7A}\cdots C^{7B}$ 0.98(2) Å.

Consideration of the covalent bond lengths, bond angles, and torsion angles in two TEG ligands of the complex cation of **I** (Tables 1–3) suggests that in these TEG ligands not only the independent atoms $C^2$ и $C^7$, but actually all their independent atoms are disordered over two positions each. However, the distances between their possibly split positions are too short to be resolved. Specifically the neglect of disordering of all the other independent nonhydrogen atoms of the two TEG ligands in the structure of **I** leads to considerable distortion of their covalent bond lengths, bond angles, and especially torsion angles. It should be noted that, in the majority of the studied crystal structures containing TEG ligands [1], the geometric parameters of these ligands are distorted similarly, i.e., the TEG ligands are disordered.

In the structure of **I**, in two TEG ligands the mean lengths of their covalent bonds (O–C 1.392±0.021 and C–C 1.472±0.005 Å) are appreciably smaller than the average statistical values: O–C($sp^3$) 1.426(11) Å for C,H–O–$CH_2$–C# fragments; C($sp^3$)–C($sp^3$) 1.524(14) Å

for C#–$CH_2$–$CH_2$–C# fragments [7]. Similar effective contraction of the covalent bonds is well known for crown ethers [3, 8], but in this structure it is enhanced by the disordering of the two TEG ligands.

As noted above, the two TEG ligands in complex **I** have the shape of a horseshoe or claw. Four O atoms of the first TEG ligand deviate from their least-squares plane by no more than ±0.081(4) Å, and the four O atoms of the second TEG ligand, by no more than ±0.020(5) Å. The angle between the least-square planes of the four O atoms of the two TEG ligands is 87.9(1)°. These two, almost perpendicular, least-squares planes pass exactly through the center of the $Mn^{2+}$ cation.

The conformations of the two TEG ligands in complex **I** are also characterized by torsion angles τ in Table 3. Generally speaking, in ordered TEG ligands all their angles τ of the O–C–C–O type should be synclinal (of the gauche type) and be in the range ±60°±20°, and all the angles τ of the C–O–C–C type should be antiperiplanar (of the trans type) and be in the range 180°±30°. As seen from Table 3, in each of the two TEG ligands of complex **I**, two independent angles τ of the type O–C–C–O are beyond this range and are smaller in the absolute value, confirming the fact that almost all the atoms of the two TEG ligands in complex **I** are disordered to a greater or lesser extent.

In the crystal structure of **I**, there are two symmetry-independent interionic (intermolecular) hydrogen bonds $O^1$–$H^1$···$Br^1$ and $O^6$–$H^6$···$Br^2$. The interatomic distances and angles corresponding to these H bonds are as follows: O–H 0.90, $H^1$···$Br^1$ 2.43, $H^6$···$Br^2$ 2.47, $O^1$···$Br^1$ 3.169(4), and $O^6$···$Br^2$ 3.189(4) Å, ∠($O^1$–$H^1$···$Br^1$) 139° and ∠($O^6$–$H^6$···$Br^2$) 137°. Because a crystallographic axis *2* passes through the center of each of the two bromide anions $Br^1$ and $Br^2$, each of them is an acceptor of two H bonds symmetrical relative to its axis *2*.

In the crystal of **I**, all the above-indicated H bonds combine the complex cations $[Mn(TEG)_2]^{2+}$ and bromide anions $Br^1$ and $Br^2$ in infinite thick layers parallel to the (*xz*) plane. The mean planes of these layers intersect crystallographic axis *y* in points ...–1/2, 0, 1/2, 1, 3/2, etc.

In the crystal structure of **I**, all the other (apart from the above-mentioned H bonds) short interionic (intermolecular) contacts are close to, or slightly shorter than the sums of the corresponding van der Waals atomic radii.

**Table 3.** Selected torsion angles (τ, deg) in the structure of **I**

| Angle | τ | Angle | τ |
|---|---|---|---|
| $H^1O^1C^{2A}C^3$ | –171 | $H^6O^6C^{7A}C^8$ | 159 |
| $H^1O^1C^{2B}C^3$ | –145 | $H^6O^6C^{7B}C^8$ | –158 |
| $O^1C^{2A}C^3O^4$ | –6(1) | $O^6C^{7A}C^8O^9$ | 45(1) |
| $O^1C^{2B}C^3O^4$ | –50(1) | $O^6C^{7B}C^8O^9$ | –33(1) |
| $C^{2A}C^3O^4C^5$ | 169(1) | $C^{7A}C^8O^9C^{10}$ | 163(1) |
| $C^{2B}C^3O^4C^5$ | –170(1) | $C^{7B}C^8O^9C^{10}$ | –155(1) |
| $C^3O^4C^5C^{5*}$ | 178(1) | $C^8O^9C^{10}C^{10*}$ | 178(1) |
| $O^4C^5C^{5*}O^{4*}$ | 31(1) | $O^9C^{10}C^{10*}O^{9*}$ | –17(1) |

## EXPERIMENTAL

Complex **I** was synthesized as follows. Triethylene glycol and manganese acetate $Mn(O_2CCH_3)_2$ in a molar ratio of 2 : 1 were dissolved in 80% aqueous ethanol, a small molar excess of concentrated aqueous HBr was added dropwise, and the mixture was allowed to evaporate at room temperature. Colorless transparent crystals of complex **I** formed on the bottom and walls of the vessel within several days.

The unit cell parameters of the crystals and the three-dimensional set of reflection intensities were obtained with an Enraf–Nonius CAD-4 automatic diffractometer (Mo$K_\alpha$ radiation, graphite monochromator). Crystals of complex **I** are rhombic: $[Mn(C_6H_{14}O_4)_2]^{2+}\cdot 2Br^-$, *M* 515.10; *a* 8.595(2), *b* 18.630(5), *c* 12.443(4) Å, *V* 1992(1) $Å^3$, *Z* 4, $d_{calc}$ 1.717 g $cm^{-3}$, μ(Mo$K_\alpha$) 47.05 $cm^{-1}$, space group $C222_1$.

The intensities of 1654 reflections ($h + k = 2n$; $2\theta \leq 60°$) were measured in the reciprocal space octant by ω/2θ scanning from a single crystal of the size 0.20 × 0.48 × 0.60 mm. The reflection intensities were then corrected for absorption by the semiempirical method [9]. After exclusion of nine systematically absent reflections, the working array of the measured $F^2(hkl)$ and $\sigma(F^2)$ included 1645 unique reflections.

The structure of **I** was solved by the direct method using the SHELXS-97 program [10] and refined by the full-matrix least-squares method (with respect to $F^2$) using the SHELXL-97 program [10] in the approximation of anisotropic thermal vibrations for the positions of all nonhydrogen atoms. For the refinement we used almost all the reflections from the working array

**Table 4.** Coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$) of the basis atoms in the crystal structure of **I**[a]

| Atom | *x* | *y* | *z* | *U*[b] |
|---|---|---|---|---|
| Br[1] | 5000 | 2395.1(4) | 2500 | 48.5(2) |
| Br[2] | 3558(1) | 5000 | 5000 | 82.6(4) |
| Mn | 0 | 3686.9(5) | 2500 | 32.3(2) |
| O[1] | 2298(4) | 3444(2) | 1766(3) | 51(1) |
| H[1] | 2757 | 3010 | 1742 | 90 |
| C[2A] | 3425(18) | 3976(6) | 1465(16) | 99(6) |
| C[2B] | 2928(14) | 3993(6) | 1131(10) | 69(4) |
| C[3] | 2826(8) | 4705(3) | 1660(7) | 67(2) |
| O[4] | 1294(5) | 4776(2) | 1991(4) | 59(1) |
| C[5] | 831(7) | 5436(3) | 2354(9) | 73(2) |
| O[6] | 1016(5) | 3906(2) | 4105(3) | 58(1) |
| H[6] | 1238 | 4345 | 4364 | 90 |
| C[7A] | 1881(15) | 3359(5) | 4669(10) | 63(3) |
| C[7B] | 809(19) | 3400(7) | 4928(11) | 72(4) |
| C[8] | 1070(9) | 2672(4) | 4510(5) | 69(2) |
| O[9] | 626(6) | 2581(2) | 3436(4) | 70(1) |
| C[10] | 241(9) | 1920(3) | 3066(5) | 89(3) |

[a] For the disordered atoms, the occupancies of the $C^{2A}$, $C^{2B}$, $C^{7A}$, and $C^{7B}$ positions are 0.50(2). [b] For nonhydrogen atoms, the equivalent parameters *U* calculated as 1/3 of the trace of the orthogonalized tensor $U_{ij}$ are given.

[including very weak reflections with $I < 2\sigma(I)$], excluding several reflections for which the measured and calculated values of $F^2$ were poorly consistent.

In the course of the structure solution and in the initial step of its refinement, we unambiguously found that one of the independent carbon atoms ($C^2$ and $C^7$) of each TEG ligand is disordered over two approximately half-occupied positions. Apparently, in the crystal of **I** not only these atoms, but also all the other independent atoms of the two TEG ligands are disordered, though to a lesser extent (see discussion above).

In the structure of **I**, all the independent H atoms at the C atoms (including disordered atoms) of the two TEG ligands were set geometrically. Their coordinates and isotropic thermal parameters were calculated using the rider model [10] in the course of least-squares refinement of the structure of **I**. The positions of the independent $H^1$ and $H^6$ atoms at the $O^1$ and $O^6$ atoms of the two TEG ligands were objectively localized by Fourier differential electron density synthesis in the intermediate step of anisotropic refinement of the structure of **I**. In the subsequent calculations, for the $H^1$ and $H^6$ atoms we used the fixed coordinates obtained from this Fourier synthesis.

For the exposed enantiomorphic crystal of **I**, we also refined by the least-squares method the absolute structure parameter: $\chi$ –0.02(2) [11]. In the last cycle of the full-matrix refinement of the structure of **I**, the absolute shifts of all the 125 varied parameters were less than $0.001\sigma$. The final coordinates and thermal parameters of the basis atoms are given in Table 4, and the site occupancies for the disordered atoms are given in the note.

The final *R*-factors are as follows: *R*1 0.039 and *wR*2 0.079 for 1200 observed reflections with $I \geq 2\sigma(I)$; *R*1 0.059 and *wR*2 0.105 for all the 1645 measured unique reflections; goodness of fit *S* 1.01 (for the definitions of *wR*2 and *S*, see [10]). In the final Fourier differential electron density synthesis, $-0.39 < \Delta\rho < 0.36e$ $Å^{-3}$. The *f*-curves used and the anomalous-dispersion corrections to them ($\Delta f'$ and $\Delta f''$) were taken from the International Tables [12].

## REFERENCES


1. Allen, F.H., *Acta Crystallogr., Sect. B,* 2002, vol. 58, no. 3/1, p. 380.
2. Rogers, R.D., Jezl, M.L., and Bauer, C.B., *Inorg. Chem.*, 1994, vol. 33, no. 25, p. 5682.
3. *Host Guest Complex Chemistry. Macrocycles. Synthesis, Structure, Applications*, Vögtle, A. and Weber, E., Eds., Berlin: Springer, 1985.
4. Shannon, R.D., *Acta Crystallogr., Sect. A*, 1976, vol. 32, no. 5, p. 751.
5. Pauling, L., *The Nature of the Chemical Bond*, New York: Cornell Univ. Press, 1960.
6. Bondi, A., *J. Phys. Chem.*, 1964, vol. 68, no. 3, p. 441.
7. Allen, F.H., Kennard, O., Watson, D.G., Brammer, L., Orpen, A.G., and Taylor, R., *J. Chem. Soc., Perkin Trans. 2*, 1987, no. 12, p. S1.
8. Van Eerden, J., Harkema, S., and Feil, D., *Acta Crystallogr., Sect. B*, 1990, vol. 46, no. 2, p. 222.
9. North, A.C.T., Phillips, D.C., and Mathews, F.S., *Acta Crystallogr., Sect. A*, 1968, vol. 24, no. 3, p. 351.
10. Sheldrick, G.M., *The SHELX-97 Manual*, Göttingen (Germany): Univ. of Göttingen, 1997.
11. Flack, H.D., *Acta Crystallogr., Sect. A*, 1983, vol. 39, no. 6, p. 876.
12. *International Tables for Crystallography*, Dordrecht (Netherlands): Kluwer Academic, 1992, Vol. C.