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An Anionic Mn(III) Ethyleneglycolate Complex

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Summary. The crystal structure of $[Na(HOCH_2CH_2OH)]_2[MnCl(OCH_2CH_2O)_2]$ consists of individual layers in which the anionic complexes form strings of vertex-sharing octahedral units. These strings are interconnected by $[Na_2(HOCH_2CH_2OH)_2]^{2+}$ units to form layers *via* Na-Cl and Na-O interactions. An outstanding feature of the compound are the unusually strong *Jahn-Teller* elongated *trans*-$[Mn(III)O_4Cl_2]$ octahedra.

Keywords. Glycolate; Manganese complexes; X-Ray structure determination; *Jahn-Teller* effect.

Introduction

The great interest in the structural chemistry of metal alkoxides is mainly due to their use in materials syntheses, mainly by sol-gel processing. The structure of the alkoxides (coordination number and geometry of the central atom) not only influences their reactivity, but also provides information on the geometry and connectivity of the building blocks in the derived materials.

Contrary to metal alkoxides with monodentate alkoxide ligands, ethyleneglycolate derivatives often exhibit multi-dimensional, polymeric crystal structures. Hydrogen bonds to co-crystallizing solvent molecules often play an important role. Examples from recent literature are $Ti(OCH_2CH_2O)_2$ [1] and various aluminum [2] and silicon ethyleneglycolates [3]. In this article, we report the crystal structure of the anionic Mn(III) ethyleneglyclolate complex $[MnCl(OCH_2CH_2O)_2]^{2-}$ which forms a layered structure through hydrogen-bond interactions with the $[Na(HOCH_2CH_2OH)]^+$ counter ions.

Results and Discussion

Upon reaction of sodium ethyleneglycolate with $MnCl_2 \cdot 4H_2O$ in ethylene glycol, reddish crystals with the shape of oblong strips were formed after prolonged standing. The composition $[Na(HOCH_2CH_2OH)]_2[MnCl(OCH_2CH_2O)_2]$ (**1**) was determined by a structure analysis. The formula implies that the central manganese atom is in the +3 oxidation state formed by air oxidation of the Mn(II) precursor.

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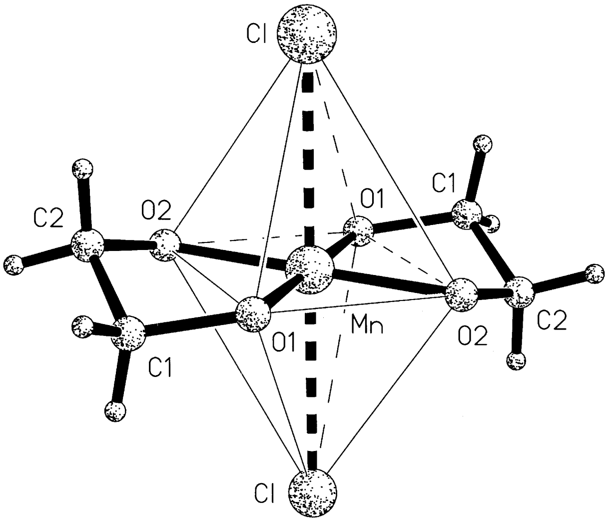

Fig. 1. Structure of the anionic complex $[MnCl(OCH_2CH_2O)_2]^{2-}$

The main characteristic of the crystal structure of **1** is the anionic complex $[MnCl(OCH_2CH_2O)_2]^{2-}$ (Fig. 1) which has a polymeric chain structure (Fig. 2). The strongly *Jahn-Teller* distorted *trans*-$[MnO_4Cl_2]$ octahedra are connected by common chlorine atoms to infinite chains parallel to (100). The short Mn-O distances of the chelating ethyleneglycolate ligands (189.4(3) and 189.7(3) pm) as well as the bond strengths calculated from them according to Ref. [4] (see Table. 1) clearly prove that the manganese atom is in the +3 oxidation state and that the ligands coordinated to the metal atom are two dianionic ethyleneglycolate ligands rather than $[HOCH_2CH_2O]^-$ or neutral ethyleneglycol ligands. This is also shown by comparison with *cis*-$[MnCl_2(HOCH_2CH_2OH)_2]$, in which the Mn(II)-O distances range from 218.4(3) to 224.7(3) pm [5].

The Mn-Cl distances (286.7(2) pm) are very long and, correspondingly, the Mn-Cl bonds very weak with only 0.14 valence units (vu) [4]. For comparison, the Mn(III)-Cl distance in tetraphenylporphyrinato complexes [MnCl(*TTP*)] with five-coordinate manganese is 230–235 pm [7] (this corresponds to bond strengths of 0.65–0.57 vu), and the Mn(II)-Cl distance in $[MnCl_2(HOCH_2CH_2OH)_2]$ with octahedral coordinaion of the metal atom amounts to 246.3(1) pm (corresponding to 0.40 vu). The strong distortion of the $[MnO_4Cl_2]$ octahedra, *i.e.* the very long Mn-Cl distance, is both due to the *Jahn-Teller* distortion of Mn(III) and the bridging bonding mode of the chlorine atoms.

Similar chain structures of corner sharing octahedra are also found in other halide-substituted Mn(III) complexes, such as $(NH_4)_2MnF_5$ (Mn-F(equatorial) 185.3(4), Mn-F(axial) 219.1(6) pm) [6]. Owing to the crystallographic symmetry, the Mn-Cl-Mn* angle in **1** is 180°, and the manganese atom is located in the plane of the four surrounding oxygen atoms.

The chains of Mn octahedra are interconnected by the $[Na_2(HOCH_2CH_2OH)_2]^{2+}$ units to form a two-dimensional layer structure (Figs. 2 and 3). Two ethyleneglycol molecules bridge two neighboring sodium ions, one oxygen atom of the

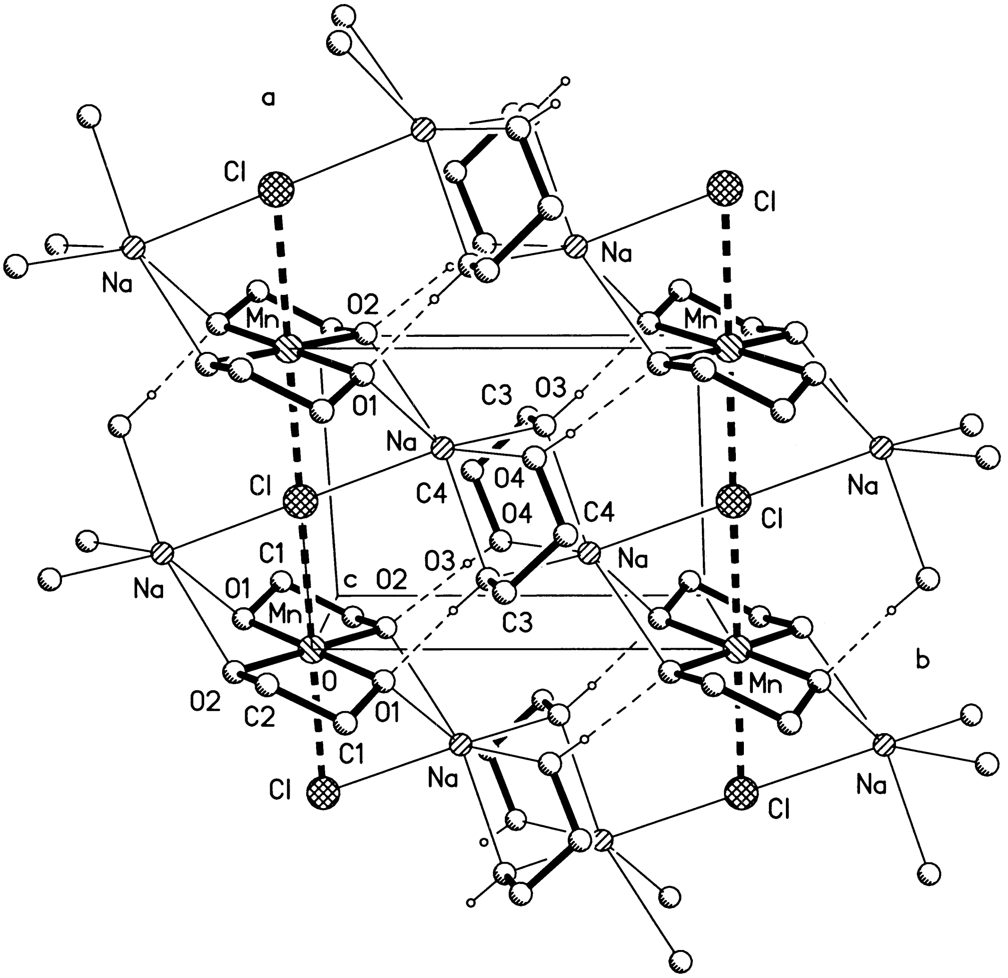

Fig. 2. View perpendicular to a layer of $[Na(HOCH_2CH_2OH)]_2[MnCl(OCH_2CH_2O)_2]$ ($z \approx 0$); the hydrogen atoms of the CH_2 groups are omitted for clarity; the thin dashed lines represent hydrogen bonds

ethyleneglycol molecules being bonded to only one Na^+ ion and the second to both Na^+ ions. In addition, each sodium ion is coordinated to the chlorine atom and two ethyleneglycolate oxygen atoms of a $[MnCl(OCH_2CH_2O)_2]^{2-}$ unit. This results in a strongly distorted octahedral coordination of each Na^+ ion (Fig. 2). The chlorine atom, located in a special crystallographic position, is in a plane with the two surrounding manganese and sodium atoms.

An important feature of the crystal structure are the hydrogen bonds between the ethyleneglycol molecules bonded to the sodium ions (O(3) and O(4) being the hydrogen donor atoms) and the oxygen atoms O(1) and O(2) of the $[MnCl(OCH_2CH_2O)_2]^{2-}$ unit. The hydrogen bonds are nearly linear (Table 1) with short $O \cdots O$ distances (268 and 267 pm) and bond strengths of about 0.2 vu. These contribute to a strengthening and stiffening of the $[Na(HOCH_2CH_2OH)]_2 \cdot [MnCl(OCH_2CH_2O)_2]$ layers oriented parallel to (001). The layers are only kept

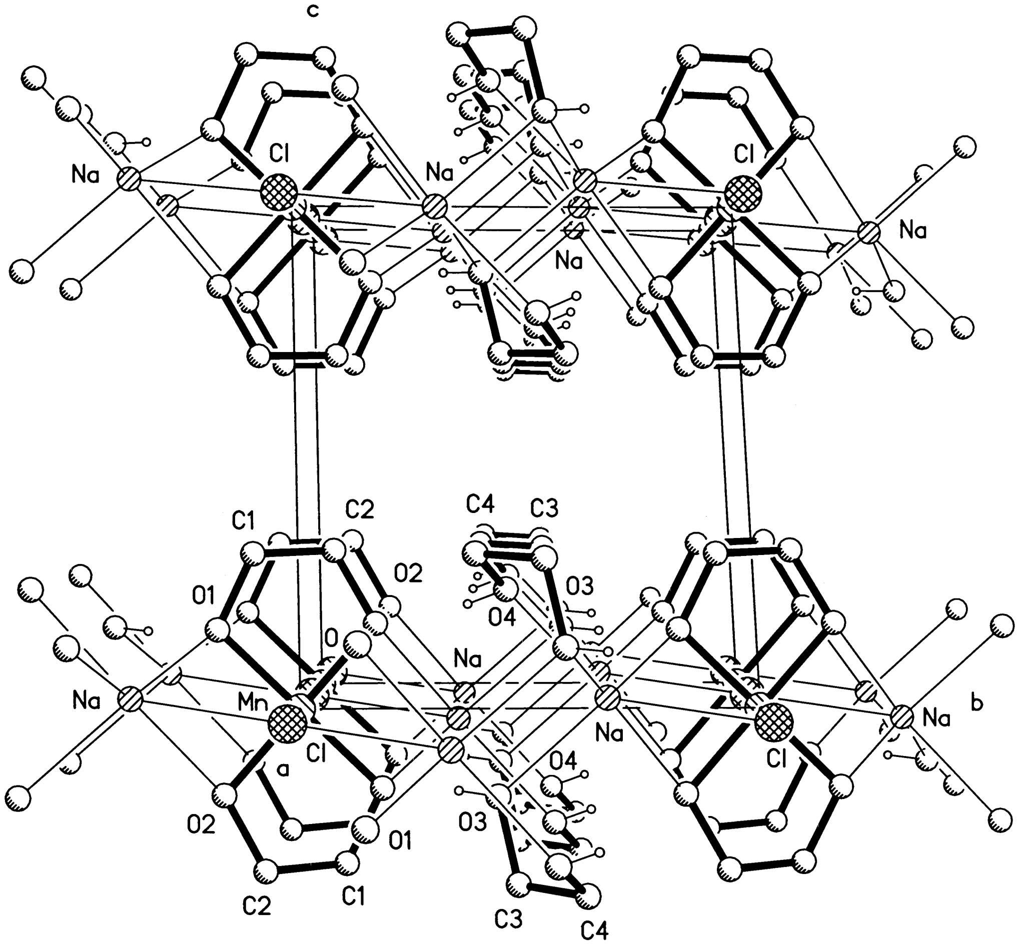

Fig. 3. Perspective drawing of the layers of **1** along (100); the hydrogen atoms of the CH_2 groups are omitted for clarity

together by *van der Waals* forces; correspondingly, the compound crystallizes in thin oblong strips.

Experimental

Synthesis of $[Na(HOCH_2CH_2OH)]_2[MnCl(OCH_2CH_2O)_2]$ (**1**)

An amount of 0.69 g (30 mmol) of sodium is added to 20 cm^3 of water-free ethyleneglycol. The mixture is stirred at room temperature until all sodium is dissolved. An amount of 1.00 g (5 mmol) of $MnCl_2 \cdot 4H_2O$ is then added, and the solution is heated to reflux until a pink precipitate is formed. After cooling to room temperature, 15 cm^3 of ethanol are added. Crystals of **1** are formed upon standing in the dark at room temperature for several weeks.

Single crystal X-ray structure analysis of **1**

Compound **1** crystallizes in thin oblong strips, which are systematically twinned parallel to their long axis. A non-twinned piece was cut off and mounted on a glass fiber. The diffraction data were

Table 1. Selected bond distances (in pm), angles (in °), and bond strengths (in vu[a]) in **1**; asterisks denote symmetry equivalence

Mn-O(1)	2x	189.7(3)	0.69	O(1)-Mn-O(2)	87.5(1)
Mn-O(2)	2x	189.4(3)	0.70	O(1)-Mn-Cl	86.5(1)
Mn-Cl	2x	286.7(2)	0.14	O(2)-Mn-Cl	96.2(1)
			Σ3.06		
Na-O(1)		236.2(3)	0.22	O-Na-O	64.4(1)–155.8(1)
Na-O(2)*		273.9(3)	0.09	O-Na-Cl	72.1(1)–139.7(1)
Na-O(3)		245.0(4)	0.17		
Na-O(3)*		237.5(3)	0.21		
Na-O(4)		242.0(4)	0.18		
Na-Cl		279.9(2)	0.17		
			Σ1.04		
C(1)-C(2)		151.2(5)		O(1)-C(1)-C(2)	107.5(4)
C(1)-O(1)		142.9(5)		C(1)-C(2)-O(2)	108.1(4)
C(2)-O(2)		142.6(5)		O(1)-C(1)-C(2)-O(2)	−47.0(5)
C(3)-C(4)		149.7(6)		O(3)-C(3)-C(4)	109.0(4)
C(3)-O(3)		143.6(5)		C(3)-C(4)-O(4)	108.6(4)
C(4)-O(4)		143.0(5)		O(3)-C(3)-C(4)-O(4)	−61.6(5)

Hydrogen bridges

$D-H\cdots A$	D–H	$H\cdots A$	$D\cdots A$	$\angle D-H\cdots A$
$O(3)\text{-}H(3)\cdots O(1)^*$	86(5)	181(5)	267.8(4)	175(4)
$O(4)\text{-}H(4)\cdots O(2)^*$	75(5)	193(5)	267.1(4)	169(5)

[a] Bond strengths in valence units calculated according to Ref. [4]

Table 2. Crystallographic data of **1**

Formula	$C_8H_{20}ClMnNa_2O_8$
Molar mass	380.6
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell	$a = 573.4(3)$ pm
	$b = 766.8(4)$ pm
	$c = 890.7(5)$ pm
	$\alpha = 91.24(2)$
	$\beta = 105.41(2)$
	$\gamma = 92.22(2)$
	$V = 377 \times 10^6$ pm^3
Z	1
Density (calc.)	1.676 g/cm^3
Absorption coefficient	1.139 mm^{-1}
F(000)	196
Crystal size	1.0 × 0.08 × 0.02 mm
θ-Range for data collection	2.4–25.0°
Number of measured reflections	4143
Number of independent reflections	1312 ($R(\text{int}) = 0.080$)
GOF (based on F^2)	0.919
R_1 (926 reflections with $F > 4\sigma(F)$)	0.046
wR_2	0.104
Max. residual electron density	0.55 e Å^{-3}

measured on a Siemens SMART diffractometer at room temperature (CCD area detector, Mo-K_α radiation, graphite monochromator, $\lambda = 71.073$ pm). Data were collected over the whole reflection sphere with 4×606 frames (ω-scans, $\Delta\omega = 0.3°$, 20 s per frame). After applying a semi-empirical absorption correction [8] the structure was solved by *Patterson* and *Fourier* syntheses. The hydrogen atoms of the CH_2 groups were calculated according to idealized geometry, the coordinates of the OH hydrogen atoms were refined. The non-hydrogen atoms were refined with anisotropic temperature parameters. All calculations were carried out with SHELX97 [9]. Selected crystallographic information is given in Table 2. Complete crystallographic data have been deposited at the Cambridge Crystallographic Data Centre. Copies can be obtained upon request (12 Union Road, Cambridge C82 IEZ, UK, fax int. code +(1223) 336–033, e-mail: teched@ccdc.cam.ac.uk) citing the deposition number CCDC 139666.

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