# Manganese(III) Formate: A Three-Dimensional Framework That Traps Carbon Dioxide Molecules**

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Of the first-row transition metals, manganese has a particularly appealing coordination chemistry due to its rich redox behavior, as demonstrated by the variety of structures and oxidation states in polynuclear manganese complexes.[1] Manganese(III) is of particular interest owing to the large magnetic anisotropy associated with its $d^4$ electron configuration, which results in high magnetoresistance and superparamagnetic-type behavior in polynuclear compounds.[2] For the synthesis of manganese(III) complexes, the reaction between permanganate and manganese(II) has been extensively used following the pioneering work of Christou et al.[3] In a different approach, Lis et al.[4] explored the reduction of $KMnO_4$ by 90% formic acid. They reported the synthesis and solid-state structure of $K_2[Mn^{II}(H_2O)_2][\{Mn^{III}_3O(HCOO)_9\}_2]$, and claimed to have obtained "manganese(III) formate" by using more concentrated acid. Although the possibility of isolating "manganese(III) formate" has been questioned,[5] this compound was also synthesized from $MnO_2$ by Weinland and Stark and was originally formulated as $Mn_3(HCOO)_9 \cdot 2H_2O$.[6]

Given our interest in the structures and electronic properties of manganese(III) complexes,[7] we synthesized "manganese(III) formate" as reported by Lis et al. by treating $KMnO_4$ with 95% formic acid at 0°C and obtained red cubes of a compound with the composition **1**. The three-dimensional polymeric framework of $Mn(HCOO)_3$ moieties in **1** acts as a host for carbon dioxide molecules produced by the reaction (1).

$Mn(HCOO)_3 \cdot \tfrac{1}{2}CO_2 \cdot \tfrac{1}{4}HCOOH \cdot \tfrac{2}{3}H_2O$ **1**

$$4H^+ + MnO_4^- + 2HCOOH \rightarrow Mn^{3+} + 2CO_2 + 4H_2O \qquad (1)$$

The presence of carbon dioxide in the solid material was first discovered by room-temperature FT-IR spectroscopy on powdered samples and subsequently confirmed by single-crystal spectroscopy. In both experiments the sharp, split asymmetric C–O stretching band was reproducibly detected at 2340 and 2362 $cm^{-1}$. The rotational lines typical of $CO_2$ in the gas phase were not resolved, and this indicates partially hindered rotation, presumably due to host–guest interactions, and excludes contamination of the sample by atmospheric $CO_2$. The vibrational spectra also indicated the presence of HCOOH and $H_2O$ molecules in the lattice.

A single-crystal X-ray investigation of **1** at 180 K revealed that each manganese ion is connected to its nearest neighbors by six bridging formate ligands (Figure 1). The resulting three-dimensional $Mn(HCOO)_3$ framework is rather open and contains two types of cages with *mmm* and $m\bar{3}$ symmetry. The residual electron density in the two types of cage was consistent with $CO_2$ and HCOOH guests, respectively. Each carbon dioxide molecule (C2–O2 1.16(1) Å)[8] interacts with the CH groups of the uncharged $Mn(HCOO)_3$ framework through four C–H···O–C–O contacts (Figure 1). The water molecules are presumably highly disordered and thus evaded X-ray detection.

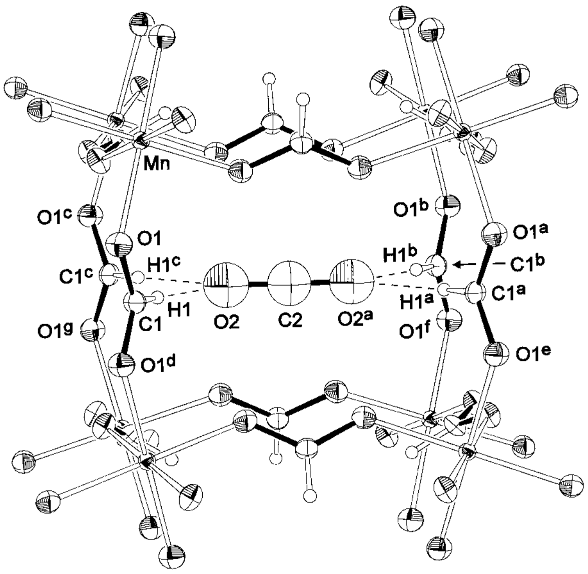

Figure 1. ORTEP plot of the cage with *mmm* symmetry in the crystal structure of **1** (30% probability thermal ellipsoids). The disordering of the $CO_2$ molecule is not shown. Selected distances [Å] and angles [°]: Mn–O1 2.001(3), C1–O1 1.244(3), H1···O2 2.66(7); O1-Mn-O1 90.0(2), O1-C1-O1$^d$ 123.4(5), H1···O2-C2 123.1(2), C1-H1···O2 177.4(2).

While several organometallic compounds containing carbon dioxide ligands are known,[9] weakly bonded $CO_2$ is exceptionally rare in solid-state structures that have been investigated by single-crystal X-ray techniques.[10, 11] In particular, host–guest interactions involving ionic coordination polymers are to our knowledge unprecedented.

An intriguing feature of the structure is the symmetry at the metal centers. The metal ion lies on a $S_6$ axis and its coordination environment is almost perfectly octahedral, in contrast with the well-known tendency of $Mn^{III}$ ions to

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undergo appreciable Jahn–Teller distortions. An absorption band in the near IR at 10900 cm$^{-1}$ might correspond to the $x^2-y^2 \leftarrow z^2$ transition of tetragonally distorted Mn$^{III}$.[7, 12] As a possible explanation, we suggest that **1** belongs to a noncubic crystal system and that the observed cubic symmetry arises from threefold merohedral twinning (see Experimental Section).

A further indication of the presence of Jahn–Teller distorted Mn$^{III}$ is provided by the magnetic properties. The $\chi T$ product increases with decreasing temperature, and above 40 K it follows a Curie–Weiss law with a ferromagnetic $\theta$ of about 19 K and a Curie constant close to that expected for a high-spin d$^4$ ion (Figure 2).[7] The sharp peak at 27 K in the plots of $\chi$ versus $T$ and $\chi T$ versus $T$ is indicative of an antiferromagnetic phase transition. The overall magnetic behavior can be rationalized in terms of a layered structure with ferromagnetic intralayer interactions and weaker antiferromagnetic interlayer interactions. Axial–equatorial exchange pathways that involve empty and singly occupied orbitals of Jahn–Teller distorted Mn$^{III}$ may provide the required intralayer coupling.[13, 14] The sudden increase of the slope in the plot of $M$ versus $B$ at 40 kOe (inset of Figure 2) is characteristic of a spin-flip transition and is therefore consistent with the presence of antiferromagnetic interlayer interactions. However, the expected saturation value of 4 $\mu_B$ for $S=2$ is not achieved even at 70 kOe. The absence of saturation might be due to the large magnetic anisotropy of manganese(III) or to the presence of a second and stronger antiferromagnetic interaction.

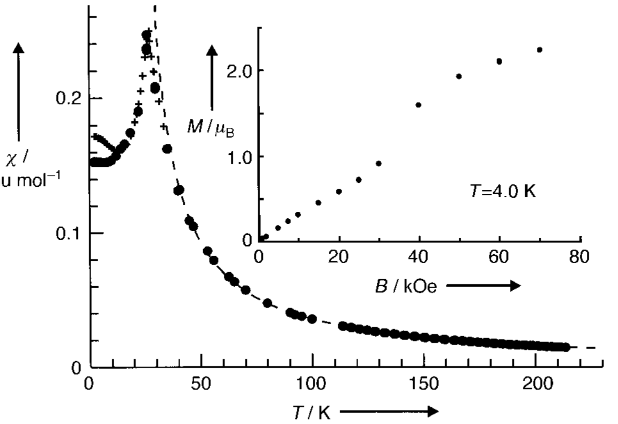

Figure 2. Plot of molar magnetic susceptibility versus temperature for **1** at 1 kOe (●) and 165 Oe (+), and Curie–Weiss plot for $C=2.91$ emu K mol$^{-1}$ and $\theta=18.7$ K (‒‒‒). The inset shows the molar magnetization at 4 K as a function of applied magnetic field.

## *Experimental Section*

Recrystallized KMnO$_4$ (0.125 g, 0.79 mmol) was added over 1 h to a stirred mixture of HCOOH (8 mL) and distilled water (0.4 mL) at 0 °C to give a red-brown solution. Stirring was continued at 0 °C for an additional 3 h, and the filtered solution was allowed to stand at 25 °C for one week. Red cubes of composition **1** and a colorless solution were recovered. The crystalline product is stable over several months if kept in the mother liquid at 4 °C. Elemental analysis was performed on a microcrystalline sample that was washed with ethanol and diethyl ether and dried under a stream of dinitrogen: found: C 19.41, H 2.13, Mn 22.7; calcd for **1**: C 19.12, H 2.07, Mn 23.32; UV/Vis/near IR (reflectance, 298 K): $\tilde{\nu}_{max}=10900, 22000$ cm$^{-1}$; FT-IR (KBr pellets, 298 K): $\tilde{\nu}=3380, 2894, 2362, 2340, 1728, 1645, 1584, 1334, 1200, 1128, 769, 761, 645, 606$ cm$^{-1}$ (unaltered after 12 h at 0.1 mmHg and 298 K); thermogravimetric analysis (10 K min$^{-1}$, 300–600 K): continuous weight loss up to thermal decomposition to Mn(HCOO)$_2 \cdot x$H$_2$O ($x \approx 0.5$) at ~480 K.

Crystal data for **1**: C$_{3.75}$H$_{4.83}$MnO$_{8.17}$, $M_r=235.52$, crystal dimensions $0.2 \times 0.2 \times 0.2$ mm, cubic, space group $Im\bar{3}$, $a=b=c=11.736(2)$ Å, $V=1616.5(5)$ Å$^3$, $Z=8$, $\rho_{calcd}=1.935$ g cm$^{-3}$, $\rho_{expt}=1.934(5)$ g cm$^{-3}$; Mo$_{K\alpha}$ radiation, $\lambda=0.71069$ Å, $\omega/2\theta$ scans, $2\theta_{max}=59.9°$, $T=180(2)$ K; 4966 reflections collected, of which 451 were independent. The data were corrected for Lorentzian and polarization effects and absorption ($\mu=1.649$ mm$^{-1}$, min./max. transmission 0.75/0.99, $\psi$ scans). The structure was solved by direct methods (SIR92[15]) and refined on $|F^2|$ by full-matrix least-squares techniques with 449 reflections and 35 parameters (SHELXL-93[16]) to give final $R1=0.0520$, $wR2=0.1264$. The formate hydrogen atom was added in an idealized position, and the C–H distance was refined. The CO$_2$ molecule was modeled over two equally populated positions related by a 0.4-Å shift along the common O-C-O axis (total occupancy 2/3 CO$_2$ per *mmm* cage). Maximum and minimum electron density 0.754 and $-0.428$ e Å$^{-3}$. The optical anisotropy of microcrystals of **1** indicates that the symmetry of the crystal lattice is intrinsically noncubic. However, the diffraction patterns of larger crystals exhibit cubic symmetry. A refinement in the orthorhombic space group *Immm* was also attempted, but neither improvement nor symmetry lowering was obtained. We suggest that the cubic diffraction symmetry is due to threefold merohedral twinning along [111], which explains the apparent absence of Jahn–Teller distortion at the metal sites. The unusual 2/3 occupancy of the *mmm* cage by CO$_2$ molecules is also consistent with this interpretation. Removal of the threefold axis leads to three inequivalent *mmm* cages, and two of them may be preferentially occupied as a result of Jahn–Teller distortion. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102134. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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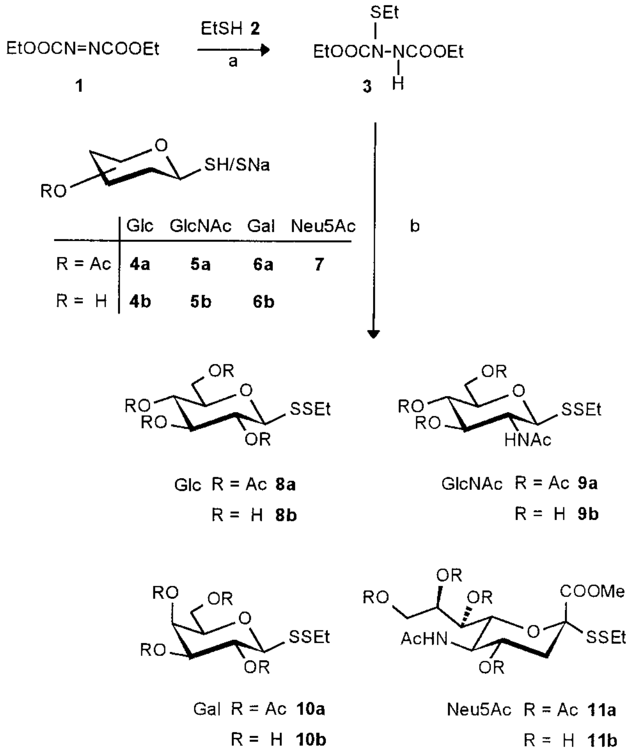
# Solid-Phase Synthesis of Thio-oligosaccharides[**]

Gerd Hummel and Ole Hindsgaul*

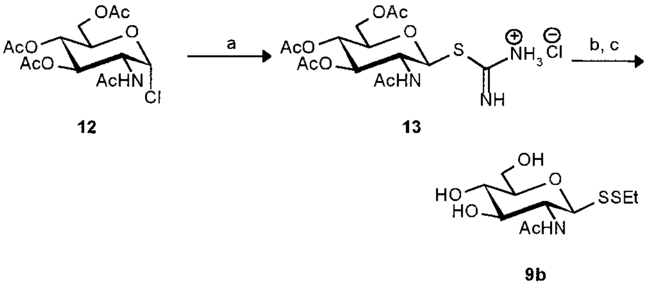
Thioglycosides are of special interest in enzyme-inhibition studies because they are much more stable to the action of glycosidases than O-glycosides and can thus inhibit enzymatic hydrolysis.[1] Thio-oligosaccharides, which contain sulfur in the glycosidic linkage, have previously been synthesized by a variety of methods including $S_N2$ displacement of a leaving group by a 1-thioglycopyranose derivative,[2] substitution of a glycosyl halide by a sugar thiolate,[3] Lewis acid catalyzed glycosylation between a glycosyl acceptor with an SH group and a glycosyl donor,[4] or Michael addition of 1-thiosugars to $\alpha,\beta$-conjugated systems.[5] These methods generally require several steps and result in low overall yield. Furthermore, the formation of unsaturated side products, loss of stereochemistry at the anomeric center, and thiol oxidation products complicate the isolation of the desired product.[6] We present here a new and efficient method for the solid-phase synthesis of thio-oligosaccharides. The key feature of this method is that a highly reactive nucleophilic sugar-1-thiolate *without protecting groups* is used as the nucleophile for coupling to trifluoromethanesulfonate (triflate)-activated glycosides. The required free thiolate is generated on the solid phase from its protected unsymmetrical ethyl disulfide.

Diethyl-*N*-(ethylsulfanyl)hydrazodicarboxylate (**3**) was prepared by the reaction of diethylazodicarboxylate (**1**) and ethanethiol (**2**) in dichloromethane (Scheme 1).[7] Compound **3** was isolated as a colorless syrup in 76% yield after column chromatography. The thiol groups of readily available protected or unprotected 1-thioaldoses (Glc, GlcNAc, Gal, Neu5Ac)[8] were selectively protected by using **3** in dichloromethane (**4a**, **5a**, **6a**, **7**) or in methanol (**4b**, **5b**, **6b**). The corresponding sugar disulfides were obtained in quantitative yields. The unprotected disulfides, obtained either directly from **4b**, **5b**, and **6b** or by deacetylation of **8a**, **9a**, **10a**, and **11a** with sodium methoxide in methanol, were used directly for immobilization on the solid phase.



Scheme 1. a) $CH_2Cl_2$, 20°C, 2 h, 75%; b) for R = Ac: $CH_2Cl_2$, THF or $CH_3CN$; for R = H: MeOH or MeOH/$H_2O$, 20°C, 5 min, 100%. Ac = acetyl.

For the preparation of larger quantities of 1-dithioethylglycosides an alternative reaction sequence was developed (Scheme 2, shown for GlcNAc). 2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-$\alpha$-D-glucopyranosyl chloride (**12**)[9] was heated with thiourea in acetone for 15 min under reflux to give **13** in 89% yield. Subsequent treatment of **13** with diethyl disulfide in methanol and triethylamine followed by deacetylation with sodium methoxide in methanol afforded the unprotected disulfide **9b** in 85% yield.



Scheme 2. a) $SC(NH_2)_2$, acetone, reflux, 15 min, 82%; b) EtSSEt, MeOH, $NEt_3$, 20°C, 2 h, 89%; c) NaOMe, MeOH, 20°C, 2 h, then $H^+$, IR-120, 96%.

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