A Novel 2D Mn(II)-Disulphide Complex $[Mn(2,2'\text{-}DTDN)(H_2O)_2]_n\cdot 2nH_2O$

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A novel two-dimensional layer manganese(II)-disulphide complex, $[Mn(2,2'\text{-}DTDN)(H_2O)_2]_n\cdot 2nH_2O$ ($DTDN^{2-}$ = dithiodinicotinate) was synthesized and characterized, in which $DTDN^{2-}$ comes from the oxidation of MNA (2-mercaptonicotinic acid) followed by a deprotonation process in aqueous solution under aerobic condition. Hydrogen bond interactions among layers lead to the formation of three-dimensional network structure.

Although numerous manganese complexes with oxygen and/or nitrogen donor atoms have been synthesized and characterized owing to their special properties and potential applications,[1] the chemistry of manganese(II)-thiolate complexes remains less developed. Some studies have shown that aromatic and aliphatic thiolates can be oxidized to disulphide complexes under suitable conditions.[2] For instances, the interaction of thiols with copper(II) leaded to the formation of disulphide complex;[3] the oxidation of thiolate to disulphide was observed in the electrochemical procedure with manganese anode.[4] As a part of our studies on metal-thiolate complexes, we recently began the works on the syntheses of manganese complexes constructed by MNA (2-mercaptonicotinic acid) ligand, which is a polyfunctional ligand possessing pyridyl N, thiolato S and carboxylic O donor atoms. Former studies illustrated that MNA consists of a mixture of neutral tautomeric or zwitterionic forms in aqueous or organic solutions, because the pK_a of the thiol group is 8.82 and that of the carboxylic group is 5.78,[5] and the possible coordination modes of MNA depend on the pH value.[6] Till now, though some complexes containing MNA ligand have been described,[7] no disulphide complex resulted from the oxidation of MNA was reported. Herein, we report a novel two-dimensional disulphide manganese complex, $[Mn(2,2'\text{-}DTDN)(H_2O)_2]_n\cdot 2nH_2O$ ($DTDN^{2-}$ = dithiodinicotinate), in which $DTDN^{2-}$ comes from the oxidation of MNA followed by a deprotonation process in aqueous solution under aerobic condition.

The reaction of $MnCl_2\cdot 4H_2O$ with excess MNA in aqueous solution yielded two kinds of crystals suitable for X-ray diffraction analysis.[8] The crystallographic analyses[9] reveal that the two complexes are the $H_2DTDN\cdot H_2O$ (**1**) and $[Mn(2,2'\text{-}DTDN)(H_2O)_2]_n\cdot 2nH_2O$ (**2**), respectively. As shown in Figure 1, **1** is an organic complex derived from the oxidation of MNA by O_2. Complex **2** is a two-dimensional layer polymer consisting of six-coordinated Mn(II) centers and uncoordinated water molecules. As shown in Figure 2, manganese(II) ion is coordinated by four oxygen atoms of the carboxylate groups from four different $DTDN^{2-}$ ligands and two oxygen atoms from coordinated water molecules in a slightly distorted octahedral coordination geometry. Four carboxylic O atoms [O(2), O(2A), O(1F), O(1D)] form the equatorial plane while the axial positions are filled by two coordination water O atoms [O(3), O(3A)]. The distances between Mn and carboxylic O atom are 2.123(2) and 2.203(2) Å, which are longer than the reported Mn-O (carboxylate group) of 1.8–2.0 Å.[10]

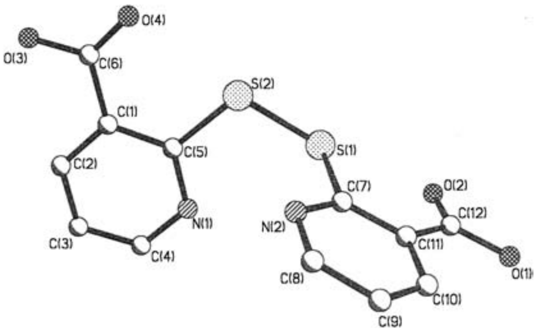

Figure 1. The structure of the Ligand $H_2DTDN\cdot H_2O$ (The hydrogen atom and the free water molecule were omitted).

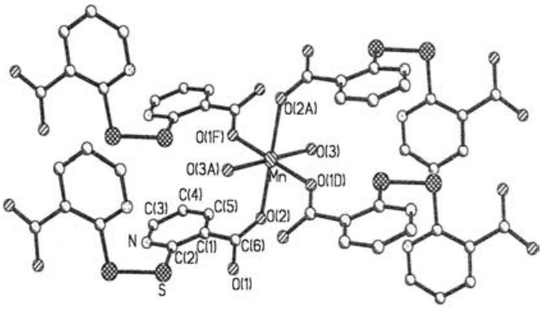

Figure 2. Local coordination environment around Mn(II) ions. Selected bond lengths (Å) and angles (°): S–S, 2.0429(18); Mn–O(1D), 2.123(2); Mn–O(1F), 2.123(2); Mn–O(2), 2.203(3); Mn–O(2A), 2.203(3); Mn–O(3), 2.221(3); Mn–O(3A), 2.221(3); C(2)–S–S, 102.96(12); O(1D)–Mn–O(1F), 180; O(1D)–Mn–O(2), 90.99(10); O(1F)–Mn–O(2), 89.01(10); O(1D)–Mn–O(2A), 89.01(10); O(1F)–Mn–O(2A), 90.99(10); O(2)–Mn–O(2A), 180; O(1D)–Mn–O(3), 86.34(13); O(1F)–Mn–O(3), 93.66(12); O(2)–Mn–O(3), 89.45(14); O(2A)–Mn–O(3), 90.55(14); O(1D)–Mn–O(3A), 93.66(12); O(1F)–Mn–O(3A), 86.34(13); O(2)–Mn–O(3A), 90.55(14); O(2A)–Mn–O(3A), 89.45(14); O(3)–Mn–O(3A), 180; C(6)–O(2)–Mn, 124.4(2).

Each $DTDN^{2-}$ ligand adopts a μ_4-bridging mode linking four Mn(II) atoms through its four carboxylic O atoms and each manganese(II) center links four $DTDN^{2-}$ ligands to give rise to a two-dimensional wave-like layer structure (Figure 3). In addition, the layers are further linked by hydrogen bonding of coordinated water molecules/uncoordinated water molecules, uncoordinated

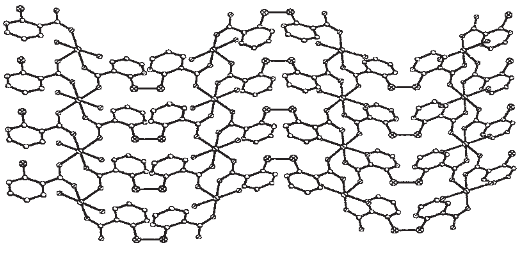

Figure 3. The two-dimensional layer structure along *a* axis.

water molecules/uncoordinated water molecules and coordinated water molecules/nitrogen atoms of the ligands to generate a three-dimensional network structure.

Temperature-dependent magnetic susceptibility measurements for complex **2** were performed on polycrystalline sample. The χ_M value increases as the temperature decreases, reaching a maximum of $0.1555\,cm^3\,mol^{-1}$ at about 8 K, and then decreases on further cooling, and the value of $\chi_M T$ is $4.033\,cm^3\,K\,mol^{-1}$ at 291 K and decreases continuously upon cooling, indicating the occurrence of antiferromagnetic interaction between the metal ions (Figure 4). According to the structural data, the complex may exhibit magnetic exchange interactions between two Mn(II) centers through short bridge via carboxolato group of $DTDN^{2-}$ (4.648 Å), actually the magnetic behavior is well interpreted based on the infinite chain model

$$\left(H = -J\sum_{i=1}^{n-1} S_{A_i}\cdot S_{A_{i+1}}\right)^{11}$$

derived by Fisher model

$$\chi_M = \frac{Ng^2\mu_B^2}{3kT}\left(\frac{1+u}{1-u}\right),$$

where $u = \coth(J/kT) - kT/J$. By using least-squares method, a very satisfied fit of the data at 5–300 K was obtained with the set of parameters of $J = -1.31\,cm^{-1}$, and $g = 1.97$, the goodness of fit *R*, defined as

$$R = \frac{\sum[(\chi_m)_i^{obs} - (\chi_m)_i^{calc}]^2}{\sum(\chi_m)_i^{obs}} \text{ is } 1.2\times10^{-7}.$$

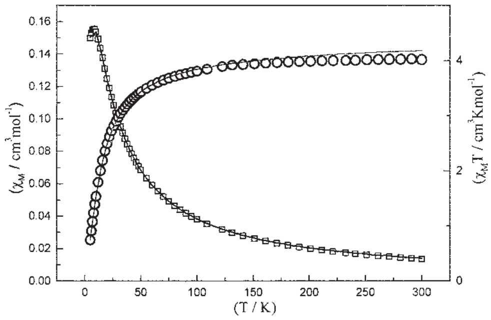

Figure 4. Experimental χ_M and $\chi_M T$ vs *T* curves for **2**. (◯)χ_m (□)χ_mT(—) the best fit obtained.

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8 Synthesis of compounds **1** and **2**: 2-HS$(C_5H_3N)CO_2H$ (0.30 g, 1.92 mmol) dissolved in 18 ml H_2O at pH 6, then 0.12 g of $MnCl_2\cdot4H_2O$ (0.61 mmol) was added and stirred for 15 min. After filtration, the resulting solution evaporated in air for five days, yellow crystals of **1** and white crystals of **2** were obtained and separated by hand. IR for **1** (KBr, cm^{-1}): 3494(m), 1699(m), 1635(m), 1562(m), 1466(m), 1400(m), 1140(vs), 1113(vs), 617(m). IR for **2** (KBr, cm^{-1}): 1587(vs), 1570(vs), 1552(vs), 1444(m), 1400(vs), 1383(vs), 1248(m), 1167(m), 1074(s), 841(m), 781(s), 723(m), 658(m), 571(m). Anal. Calcd. for **2** (%): C, 33.26; H, 3.26; N, 6.47%. Found: C, 33.30; H, 3.17; N, 6.46%.

9 Crystal data for **1**: crystal dimensions $0.41\times0.13\times0.09$ mm, formula $C_{12}H_{10}N_2O_5S_2$, fw = 326.34, monoclinic, space group $P21/c$, $a = 5.5590(16)$ Å, $b = 30.227(14)$ Å, $c = 8.0589(6)$ Å, $\beta = 101.874(2)^\circ$, $V = 1325.2(7)$ Å^3, $Z = 4$, $T = 293(2)$ K, $D_{calc} = 1.636\,g/cm^3$, No. of used data ($I_O > 2\sigma(I)$) = 3032, $R = 0.0728$, $R_W = 0.1690$. Crystal data for **2**: crystal dimensions $0.46\times0.12\times0.10$ mm, formula $C_{12}H_{14}MnN_2O_8S_2$, fw = 433.32, monoclinic, space group $C2/c$, $a = 20.6467(10)$ Å, $b = 4.6483(2)$ Å, $c = 18.5845(12)$ Å, $\beta = 116.287(2)^\circ$, $V = 1599.15(15)$ Å^3, $Z = 4$, $T = 293(2)$ K, $D_{calc} = 1.800\,g/cm^3$, No. of used data ($I_O > 2\sigma(I)$) = 2307, $R = 0.0425$, $R_W = 0.1046$. Detail crystallographic data of **1** and **2** has been deposited at the Cambridge Crystallographic Data Center (CCDC-176908 for **1** and 175388 for **2**). The intensity data were collected on a Siemens Smart CCD diffractometer with graphite-monochromated Mo-Kα($\lambda = 0.71073$ Å) radiation at room temperature. The structures were solved by directed methods and the positions of H atoms were generated from difference Fourier maps. All of the calculations were performed on a Legand computer by using the SHELXTL-93 program package.

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