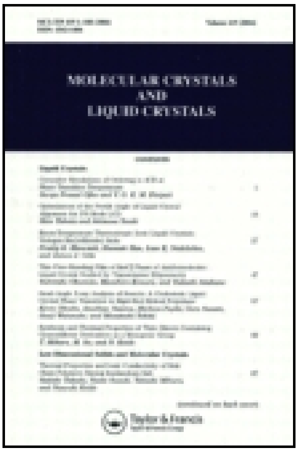

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One-Dimensional Manganese Assembled Compounds of Bromanilic Acid and Nitranilic Acid

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One-Dimensional Manganese Assembled Compounds of Bromanilic Acid and Nitranilic Acid

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Two one-dimensional manganese assembled compounds of the general formula $[Mn(L)(terpy)]_n$ (L = bromanilate, BA^{2-} (**1**) and nitranilate, NA^{2-} (**2**); terpy = 2,2':6',2"-terpyridine) have been synthesized and characterized by single crystal X-ray diffraction. Compound **1** crystallizes in the triclinic, space group $P\overline{1}$ (#2), with a = 10.221(1) Å, b = 10.335(1) Å, c = 10.200(1) Å, α = 96.77(1)°, β = 113.74(1)°, γ = 85.52(1)°, V = 978.9(2) Å^3, Z = 2. Compound **2** crystallizes in the triclinic, space group $P\overline{1}$ (#2), with a = 10.124(3) Å, b = 10.929(4) Å, c = 9.828(2) Å, α = 96.17(3)°, β = 98.19(3)°, γ = 66.16(2)°, V = 983.0(6) Å^3, Z = 2. In both the compounds manganese (II) ions are hepta-coordinated making zigzag chains. BA^{2-} and NA^{2-} bridges the Mn(II) ions in **1** and **2**, respectively, whereas terpy coordinates as a neutral terminal ligand.

Keywords bromanilic acid; nitranilic acid; 2,2':6',2"-terpyridine; manganese(II); one-dimensional compound.

INTRODUCTION

Metal assembled one-dimensional compounds are of great interest in the field of molecule-based magnetic materials, because these compounds occupy an intermediate situation between magnetic clusters of high nuclearity and three-dimensional extended lattices.[1] One-dimensional magnetic systems provide excellent examples on which the development of suitable theoretical models affords a better understanding of the exchange interactions in extended lattices.[2] 2,5-dihydroxy benzoquinone derivatives can be used as bis-bidentate ligand, therefore, they are the good candidates to construct one-dimensional hybrid compounds of transition metal ions. A series of novel one-dimensional compound of chloranilic acid have been constructed by the self-assembled technique and their magnetic susceptibilities are measured.[3-5] However, compounds with the similar ligands, bromanilic acid and nitranilic acid of the same family are not well explored. To construct one-dimensional compounds, one of the strategies is to maintain the metal coordination environment to retard the chain from further bridging. In this context, usage of mixed organic ligands facilitates to get the desired dimensionality. Usually terminal ligands retain the chain structure. In this research, two one-dimensional manganese assembled compounds of bromanilic acid and nitranilic acid, $[Mn(L)(terpy)]_n$ (L = bromanilate, BA^{2-} (**1**) and nitranilate, NA^{2-} (**2**)) are synthesized with the help of terpyridine. Crystal structures and packing arrangements of the two compounds are described here.

EXPERIMENTAL

Syntheses

$[Mn(BA)(terpy)]_n$ **1**. To the solution of terpyridine (0.116 g) in 1:1 (v/v) $EtOH/H_2O$ (100 mL), manganese chloride hexahydrate (0.063

g) was mixed. After stirring few minutes an yellow powder of Mn(terpy)Cl_2 was precipitated out from the mixture (yield 85%). Then an aqueous solution of Mn(terpy)Cl_2 (0.1 mmol) was added to a solution of the sodium salt of bromanilic acid (0.1 mmol) in 1:1 (v/v) EtOH/H_2O in the tubes without mixing the two solutions. Red plate like crystals began to form in a month. Anal. Calcd. for $MnC_{21}O_4Br_2N_3H_{11}$: C, 43.18; H, 1.90; N, 7.19. Found: C, 42.92; H, 2.00; N, 8.62.

$[Mn(NA)(terpy)]_n$ **2**. An aqueous solution of $Na_2NA.nH_2O$ (0.1 mmol) was transferred to a glass tube, then an aqueous solution of Mn(terpy)Cl_2 (0.1 mmol) was poured into the tube without mixing the solutions. Red plate crystals began to form at ambient temperature in a month. Mn(terpy)Cl_2 is prepared using the same procedure as in **1**. Elemental analysis of **2** was not carried out to avoid any explosion due to the presence of nitro group in the ligand.

Crystallographic Data Collection and Refinement of the Structures

A suitable crystal was chosen and mounted on glass fiber with epoxy resin. Data collection of compound **1** and **2** was carried out on a Rigaku AFC7R diffractometer. The structure was solved by direct methods (Rigaku TEXSAN crystallographic software package of Molecular Structure Corporation). Full-matrix least-squares refinements were carried out with anisotropic thermal parameters for all non-hydrogen atoms. The final cycle of full-matrix least-squares refinement was based on No and n variable parameters and converged with unweighted agreement factors of $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $Rw = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$ where $w = 1/\sigma^2(F_o) = [\sigma_c^2(F_o) + p^2/4\ F_o^2]^{-1}$. Crystal Data of **1**. $MnC_{21}O_4Br_2N_3H_{11}$, fw = 584.08, triclinic, space group $P\bar{1}$ (#2), with $a = 10.221(1)$ Å, $b = 10.335(1)$ Å, $c = 10.200(1)$ Å, $\alpha = 96.77(1)°$, $\beta = 113.74(1)°$, $\gamma = 85.52(1)°$, $V = 978.9(2)$ Å^3, $Z = 2$, $T = 23°C$, μ(MoKα) = 48.05 cm^{-1}, λ(Mo Kα) = 0.71069 Å, $n = 281$; N, No ($I > 3\sigma(I)$) = 4503, 2916; R, Rw = 0.032, 0.027. Crystal Data of **2**. $MnC_{21}O_8N_5H_{11}$, fw = 516.28, triclinic, space group $P\bar{1}$ (#2), with $a = 10.124(3)$ Å, $b = 10.929(4)$ Å, $c = 9.828(2)$ Å, $\alpha = 96.17(3)°$, $\beta = 98.19(3)°$, $\gamma = 66.16(2)°$, $V = 983.0(6)$ Å^3, $Z = 2$, $T = 23°C$, μ(MoKα) =

7.38 cm^{-1}, λ(Mo Kα) = 0.71069 Å, n = 361; N, No ($I > 3\sigma(I)$) = 4503, 3328; R, Rw = 0.039, 0.039.

CRYSTAL STRUCTURES

[Mn(BA)(terpy)]$_n$ **1**. The structure of the compound **1** is made up of neutral [Mn(BA)(terpy)] units. This unit consists of hepta-coordinated manganese(II) ion in which the coordination sites are

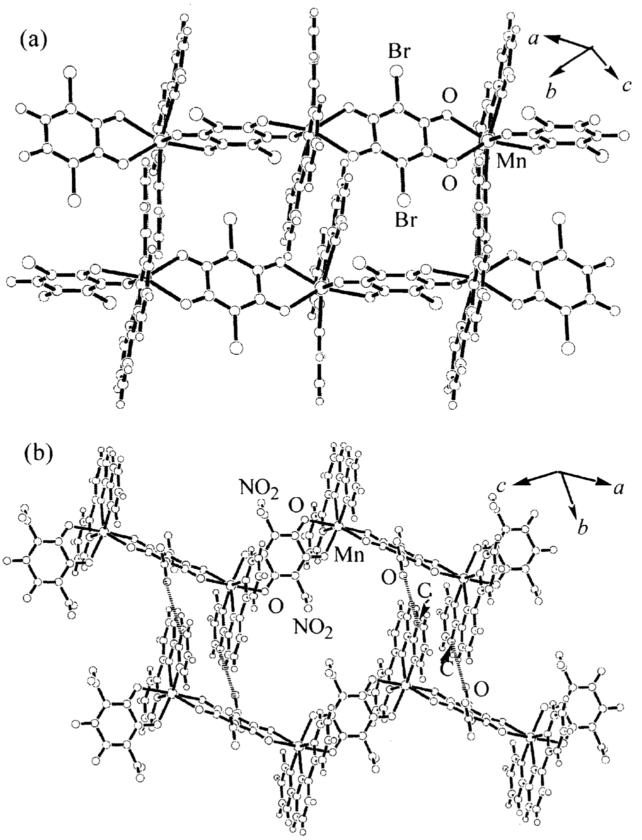

Figure 1. Crystal packing structure of **1** (a) and **2** (b). The dashed lines represent CH---O interaction (C---O distance: 3.21 Å).

occupied by four oxygen atoms from the two BA^{2-} and three nitrogen atoms of one terpy ligands. The geometry around the Mn(II) ion is not ideally pentagonal bipyramidal[6] as found for seven coordinated Mn(II) ions, rather distorted. The BA^{2-} bridges Mn(II) ions, which leads to infinite chain exhibiting a zigzag pattern along the [100] plane with terpyridine ligands stacking between the chains (Fig. 1(a)). The nearest C-C distance of the stacked terpyridine ligands is 3.41 Å. This stacking interaction makes the three dimensional packing structure. There are two types of BA^{2-} in the chain, but Mn-Mn distances through the BA^{2-} are almost the same; average distance is 8.39 Å. The pattern of the chain and the average Mn-Mn distance is same as found in the manganese assembled compound of chloranilic acid and terpy.[4] However, the Mn-Mn separation in **1** is larger than that of the CA^{2-} bridged compound, $\{[Mn(CA)(H_2O)_2](H_2O)\}_n$ (8.20 Å) and same of $[Mn(CA)(terpy)]_n$.[3,4] The nearest distance between the two manganese ions of two neighbouring chains is 7.25 Å. Two BA^{2-} rings around a manganese ion in **1** are not parallel, dihedral angle being 102.86°.

$[Mn(NA)(terpy)]_n$ **2**. The structure of the compound **2** is made up of neutral [Mn(NA)(terpy)] units. Each manganese(II) ion is also hepta-coordinated; four oxygen atoms from two NA^{2-} and three nitrogen atoms of one terpyridine. The geometry around the Mn(II) ion is similar to that of **1**. The NA^{2-} bridges manganese (II) ions, which leads to infinite chains exhibiting a zigzag pattern along [011] plane (Fig. 1(b)). The Mn-Mn separation (8.54 Å) in the chain is higher than that of **1** (8.39 Å). A little difference in the pattern of the chain is observed in **2**, which is attributed from the dihedral angle (68.83°) of the two planes of CA^{2-} coordinated to the same manganese ion and the distance between the nearest Mn-Mn distance (7.72 Å) of the neighbouring chains. Mn-O bond distances of both the compounds are very similar to each other (average distance 2.27 Å for **1** and 2.29 Å for **2**) but higher than that of the chloranilate bridged compound (average distance 2.18 Å).[7] Stacking interaction between terpy rings (3.26 Å) and CH---O interaction between the C of terpy and O atom of NO_2 in NA^{2-}(C---O distance: 3.21 Å) make the packing structure of **2**.

CONCLUSION

In conclusion, we have been able to show that terpyridine is a good terminal ligand to get bromanilate and nitranilate bridged one-dimensional compounds of manganese ions. The effect of substituents in the 3,6 positions of the two ligands does not influence strongly on their dianionic forms to get one-dimensional structures. Finally, π-π stacking interaction play an important role in controlling the packing structure of metal-organic hybrid compounds.

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REFERENCES

1. O. Kahn, Molecular Magnetism, VCH Publishers, New York (1993).
2. J. J. Borrás-Almenar, E. Coronado, J. Curely, R. Georges, and J. C. Gianduzzo, Inorg. Chem., **33**, 5171 (1994).
3. S. Kawata, S. Kitagawa, H. Kumagai, T. Ishiyama, K. Honda, H. Tobita, K. Adachi, and M. Katada, Chem. Mater., **10**, 3902 (1998).
4. M. K. Kabir, M. Kawahara, H. Kumagai, K. Adachi, S. Kawata, T. Ishii, and S. Kitagawa, Polyhedron, **20**, 1417 (2001).
5. S. Kawata, S. Kitagawa, H. Kumagai, C. Kudo, H. Kamesaki, T. Ishiyama, R. Suzuki, M. Kondo, and M. Katada, Inorg. Chem., **35**, 4449 (1996).
6. G. J. Palenik, and Wester, D. W., Inorg. Chem., **17**, 864 (1978).
7. L.-M. Zheng, H. W. Schmalle, R. Huber, and S. Decurtins, Polyhedron, **15**, 4399 (1996).