Crystal structure of bis(μ-4,4′-bipyridyl-N,N′)-tetakis(cyanoaceto)dimanganese(II) tetrahydrate, Mn₂(C₃H₂NO₂)₄(C₁₀H₈N₂)₂ ⋅ 4H₂O

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Abstract

C₃₂H₃₂Mn₁₂N₈O₁₂, orthorhombic, Pccn (no. 56), a = 13.028(2) Å, b = 19.081(3) Å, c = 7.261(1) Å, V = 1805.0 Å³, Z = 2, Rₚ(F) = 0.029, wR²(F²) = 0.075, T = 291 K.

Source of material

Mn(CH₃COO)₂ ⋅ 4H₂O (0.123 g, 0.5 mmol) and 4,4′-bipyridine (0.96 g, 0.5 mmol) were refluxed in anhydrous methanol (10 ml) for 50 min, then, cyanoacetic acid (0.88 g, 1 mmol) was added. The pH value was adjusted to 3 with 0.5 M CH₃COOH solution. The mixture was further stirred for 2 h, then filtered. The resulting clear solution was diffused with diethyl ether vapor at room temperature for two weeks. Dark green crystals were obtained, collected by filtration and dried in air (yield, 0.156 g, 37 %).

Elemental analysis — found: C, 46.48 %; H, 34.59 %; N, 13.46 %; calculated for C₃₂H₃₂N₈O₁₂Mn₁₂: C, 46.27 %; H, 34.88 %; N, 13.49 %. IR data are available in the CIF.

Experimental details

The positions of the water hydrogen atoms were found from Fourier difference synthesis and refined isotopically. The remaining hydrogen atoms were generated theoretically, and included as fixed contributions without further refinement.

Discussion

The chemistry of complexes with multidentate ligands such as 4,4′-bipyridine have gained much interest because of their use as models in biological systems, organic reactions, and as fluorescent materials [1-4]. 4,4′-Bipyridine is an excellent rod-like bifunctional ligand. It has been extensively employed as the rigid organic building block for the construction of the infinite 1D, 2D, 3D atomic arrangements [5-7]. Manganese is an essential trace element, forming the active sites in metalloproteins [8]. Potential importance of manganese complexes is evidenced as active site in photosystem II (PSII) which is a tetranuclear manganese complex [9]. It plays a vital role in many enzymatic systems such as superoxide dismutase, peroxidase, dioxygenase and catalase where mononuclear manganese active centers are present [10]. The title crystal structure consists of manganese complexes with cyanoacetic acid anions, bridged via 4,4′-bipy molecules, with the Mn-Mn separation of 11.558 Å. The Mn(II) ions are coordinated with two cyanoacetic acid, two waters and two 4,4′-bipyridine molecules. The Mn(II) ions adopt a distorted octahedral coordination Ν₂Θ₄, maybe due to the Jahn-Teller effect. The two oxygen atoms are from the coordinated water molecules, the other two oxygen atoms are from the cyanoacetic acid anions, and two nitrogen atoms are from two 4,4-bipyridine molecules, respectively. The nitrogen atoms from the 4,4′-bipy molecules are located in the axial positions, the oxygen atoms occupy the equatorial positions. The cyanoacetic acid anions display the monodentate coordination fashion, while the 4,4′-bipy molecules adopted a bidentate coordination mode. The bond distances of Mn₁—N₁, Mn₁—O₂, Mn₁—O₃ are 2.256(1) Å, 2.177(1) Å, 2.235(2) Å, respectively, being in the range found for other Mn complexes [11,12]. The N₁′—Mn₁—N₁ group and the O₂′—Mn₁—O₂ group are linear by symmetry. The torsion angles of O₂′—Mn₁—O₂—C₆, O₃′—Mn₁—O₂—C₆, O₃′—Mn₁—O₂—C₆, and N₁′—Mn₁—O₂—C₆ are 119(3)°, 22.2(2)°, -157.8(2)°, -66.7(2)°, respectively (symmetry code i: -x,-y,-z). The pyridinyl ring C₁—C₂—C₃—C₄—C₅—N₁ is almost planar with the average deviation from the ring plane is 0.054 Å, and the maximum deviation are -0.081 Å for N₁, and +0.006 Å for C₁A, respectively.

The three-dimensional supramolecular framework is constructed by hydrogen bonds O—H(W)—O linking the neighboring molecules. Both kinds of hydrogen bonds O₃—H₁W—O₁, [O₃—H₁W—O₁ = 2.679(2) Å, 167(2)°], and O₃—H₂W—O₁, [O₃—H₂W—O₁ = 2.934(2) Å, 146(2)° (symmetry code ii: -x,-y,-z)] are formed by the oxygen atoms from cyanoacetic acid anions. Several one-dimensional channels along [010] are formed by the 4,4′-bipy molecules and cyanoacetic acid anions.
Table 1. Data collection and handling.

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References