Crystal structure of tetraaquae-2,2'-bipyridinemanganese(II) 4-(sulfonylglycine)benzoic acid, [Mn(H$_2$O)$_4$(C$_{10}$H$_8$N$_2$)][C$_{10}$H$_7$NO$_6$S]

Wen-Ying Zhang* and Shuai Yuan

Chongqing University of Post and Telecommunication, College of Bio-Informatics, Chongqing 400065, P. R. China

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Abstract

C$_{19}$H$_{23}$MnN$_3$O$_{10}$S, triclinic, $P\overline{1}$ (no. 2), $a = 7.639(1)$ Å, $b = 13.161(2)$ Å, $c = 13.245(2)$ Å, $\alpha = 64.329(2)$°, $\beta = 73.977(2)$°, $\gamma = 86.683(2)$°, $V = 1150.6$ Å$^3$, $Z = 2$, $R(F) = 0.045$, $wR_{	ext{ref}}(F^2) = 0.1145$, $T = 273$ K.

Source of material

A mixture of Mn(ClO$_4$)$_2$·6H$_2$O (0.19 g, 0.5 mmol) and 4-(sulfonyl-glycine)benzoic acid (H$_3$L, 0.14 g, 0.5 mmol) was stirred to 15 ml aqueous solution. The solution was adjusted to pH = 5 with 1 M NaOH. Then 3 ml ethanol solution of bipy (0.19 g, 1 mmol) was added. The reaction mixture was heated on a water bath for 14 h at 65 °C, and then filtered. Yellow crystals of the title compound were separated from the mother liquor by slow evaporation of the solvent at room temperature after one week. Elemental analysis — found: C, 42.31 %; H, 4.39 %; N, 7.62 %; calculated for C$_{19}$H$_{23}$MnN$_3$O$_{10}$S: C, 42.22 %; H, 4.29 %; N, 7.78 %.

Discussion

The rational design and synthesis of new extended supramolecular networks are of great interest and have brought forth diversities of frameworks with fascinating structural motifs [1-5]. In general, the metallosupramolecular systems may display a variety of useful physicochemical properties and thus potential applications in the scopes of catalysis, molecular recognition, etc. So far many infinite 1D, 2D and 3D supramolecular frameworks have accomplished. Their primary structural motifs are dominated by metal-ligand coordinative bonds, and in this context, the design of suitable organic ligands is of the most importance. Beyond the robust metal-ligand coordination, other non-covalent bonding forces have also been proven to be powerful tools for the fine-tuning of functional architectures [6-9]. These weak secondary interactions, such as hydrogen bonds, π-π stacking and van der Waals forces, make the molecular assembly reversible and variable, and provide synthetic flexibility and functional diversity. On the other hand, the metal carboxylates have been shown to be an important family of MOFs, and have continuously received great attention for decades due to their excellent coordination capability and the possibility to synthesize new functional materials [10-16]. Compared to other carboxylate ligands, 4-(sulfonyl-glycine)benzoic acid does not only contain two bridging carboxylate moieties but possess another two potential groups, i. e., the nitrogen atoms and oxygen atoms of sulfonate. This asymmetric geometry may produce unique structural motifs with beautiful aesthetics and useful functional properties. It can act not only as a hydrogen bond acceptor but also as a hydrogen bond donor, depending upon the degree of deprotonation. The title crystal structure comprises a [Mn(bipy) (H$_2$O)$_4$]$^{2+}$ cation and a HL$^{2-}$ dianion in an asymmetric unit. The Mn(II) ion is six-
coordinated (MnN₂O₃) and the coordination polyhedron is a distorted octahedral geometry (figure, top). The bond lengths of Mn₁—O are in the range of 2.129(2)–2.203(2) Å. The bipy molecule serves as bidentate ligand chelating to the Mn(II) ion with Mn₁—N₁ and Mn₁—N₂ bond distances of 2.280(2) Å and 2.258(2) Å, respectively. Although HL⁺ does not coordinate the metal atoms, each HL⁺ group is involved in quaternary-cyclic intensely intramolecular hydrogen-bonding interactions with coordinated water molecule through its two carboxylate groups. At last, these cation-anion species are organized into a two-dimensional supramolecular architecture (figure, bottom). The bond lengths and angles of these hydrogen bonding parameters are in the range of 2.652(3)–2.741(3) Å and 151.7–171.6°, respectively. The degree of deprotonation of HL⁺ plays an important factor for the formation of the complex.

### Table 1. Data collection and handling.

| Crystal: | yellow block, size 0.07 x 0.11 x 0.25 mm |
| Wavelength: | Mo Kα, radiation (0.71073 Å) |
| µ: | 7.25 cm⁻¹ |
| Diffraconometer, scan mode: | Bruker SMART CCD, ϕ/ω |
| 2θmax: | 55° |
| N(hkl measured), N(hkl unique): | 10295, 5207 |
| Criterion for Iobs, N(hkl): | Iobs > 2σ(Iobs), 3400 |
| Programs: | SHELXS-97 [17], SHELXL-97 [18], SHELXL [19] |

### Table 2. Atomic coordinates and displacement parameters (in Å²).

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### Table 3. Atomic coordinates and displacement parameters (in Å²).

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**Note:** The tables contain detailed atomic coordinates and displacement parameters, which are crucial for understanding the crystal structure and its interactions. The data includes bond lengths, angles, and other geometric parameters that help in visualizing the molecular arrangement and its properties.
References


