Crystal structure of (1,10-phenanthroline-κ²N,N′)-bis(1H-pyrazole-3-carboxylato-κ²N,O)manganese (II) trihydrate, C₂₀H₂₀N₆O₇Mn

Abstract

C₂₀H₂₀N₆O₇Mn, monoclinic, P2₁/c (no. 14), a = 10.3170(9) Å, b = 13.1061(12) Å, c = 17.6919(15) Å, β = 108.231(3)°, V = 2272.1(3) Å³, Z = 4, R₁(F) = 0.0428, wR₂(F²) = 0.1058, T = 298 K.

CCDC no.: 1541178

The crystal structure is shown in the figure. Hydrogen atoms are omitted for clarity. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

<table>
<thead>
<tr>
<th>Crystal:</th>
<th>Yellow block</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size:</td>
<td>0.40 × 0.37 × 0.25 mm</td>
</tr>
<tr>
<td>Wavelength:</td>
<td>Mo Kα radiation (0.71073 Å)</td>
</tr>
<tr>
<td>µ:</td>
<td>6.4 cm⁻¹</td>
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<tr>
<td>Diffractometer, scan mode:</td>
<td>Bruker SMART, φ and ω</td>
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<tr>
<td>2θ_max, completeness:</td>
<td>50°, &gt;99%</td>
</tr>
<tr>
<td>N(hkl)_measured, N(hkl)_unique, R_int:</td>
<td>11134, 4006, 0.041</td>
</tr>
<tr>
<td>Criterion for Iobs, N(hkl)_gt:</td>
<td>Iobs &gt; 2σ(Iobs), 2610</td>
</tr>
<tr>
<td>N(param)_refined:</td>
<td>307</td>
</tr>
<tr>
<td>Programs:</td>
<td>Bruker programs [10], SHELX [11]</td>
</tr>
</tbody>
</table>

Source of material

All reagents and solvents employed are commercially available and used as received. A mixture of pyrazolecarboxylic acid (H₂pca) (0.0224 g, 0.2 mmol), Mn(OAc)₂·4H₂O (0.0245 g, 0.1 mmol), phenanthroline (phen) (0.0198 g, 0.1 mmol) and distilled water (10 mL) was sealed in a 23 mL Teflon-lined steel vessel (pH 4.4) and heated at 180 °C for 72 h, then cooled to room temperature at a rate of 0.1 °C min⁻¹. The resulting yellow block crystals were washed with distilled water. The yield is ca. 35% based on Mn.

Experimental details

H atoms attached to C atoms were placed in geometrically idealized positions (C—H 0.93 Å) and treated as riding on their parent atoms, with Uiso(H) = 1.2Ueq(C). The water H-atoms were located in a difference Fourier map, and were defined with distance restraint of O—H = 0.82 Å and Uiso(H) = 1.5Ueq(O).

Discussion

The assembly of supramolecular architectures based on non-covalent interactions has been developed in the field of supramolecular chemistry and crystal engineering [1–3]. The hydrogen bond interactions as a kind of non-covalent interactions play an important role in forming various supramolecular frameworks. The hydrogen bond interactions...
not only expand the low structures through the effect of connection, but also generate the diverse water clusters, such as tetramers, pentamers, hexamers, octamers and decamers [4–7]. On the other hand phenanthroline complexes are well known for decades [8] and are still of general interest [9].

As shown in the figure, the N-donor ligand phen is introduced into the Mn—Hpca system. There is one Mn$^{2+}$ cation, one phen ligand, two Hpca$^{-}$ anions and three lattice water molecules in a asymmetric unit. The Mn$^{2+}$ center shows a distorted (MnO$_6$N$_4$) octahedral coordination geometry with two nitrogen atoms (N1, N3) from two Hpca$^{-}$ anions, two chelate nitrogen atoms (N5, N6) from one phen ligand and two carboxylic oxygen atoms (O1, O3) from two Hpca$^{-}$ anions. The distances of the Mn—O and Mn—N are 2.154(2)–2.173(2) Å and 2.232(3)–2.295(3) Å, respectively. The bond angles around Mn$^{2+}$ ion are in the range of 73.2(1)–167.5(1)$^\circ$. Both Hpca$^{-}$ anion and phen ligand coordinate as chelate ligands to form three five-membered rings. The lattice water molecules are creating several hexanuclear chair-like water clusters by the hydrogen bonding interaction with the O6—H6D···O7, O7—H7C···O8 and O7—H7D···O5 and O7—H7D···O5 distances of 2.752(4) Å, 2.880(2) Å and 2.724(5) Å, respectively. A final three-dimensional framework is formed by the oxygen atoms (O5, O6) of the hexanuclear water clusters and the carboxylic oxygen atoms (O1, O2, O4) and the pyrazole nitrogen atoms (N2) from Hpca$^{-}$ (O5—H5D···O4 = 2.759(0) Å, O5—H5C···O1 = 2.738(9) Å, O6—H6C···O2 = 2.697(2) Å, N2—H2···O6 = 2.654(9) Å).

Acknowledgements: This work was supported by the Program for National Natural Science Foundation of China (Nos. 21271024 and 20971014) and Beijing Natural Science (No. 2112037).

References


pillars between n–stacked and H–bonded sheets of (m-
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