Crystal structure of diaquabis(2-ethyl-4-carboxylato-5-carboxy-1*H*-imidazole-κ^2N^3,O^4)manganese(II) — water (1:3), $[Mn(H_2O)_2(C_7H_7N_2O_4)_2] \cdot 3H_2O$

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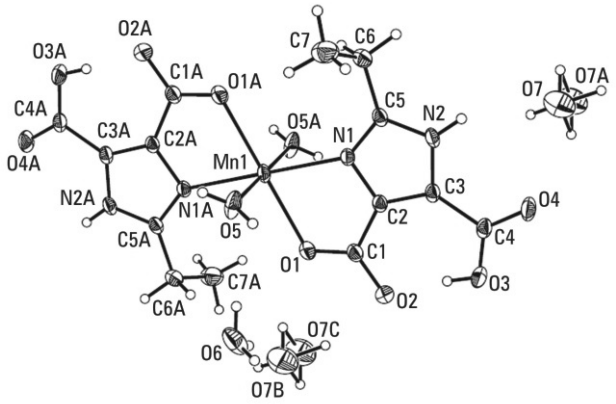

Abstract

$C_{14}H_{24}MnN_4O_{13}$, triclinic, $P\bar{1}$ (no. 2), a = 7.2920(8) Å, b = 8.964(1) Å, c = 9.510(1) Å, α = 64.269(1)°, β = 88.749(2)°, γ = 71.840(1)°, V = 527.4 Å^3, Z = 1, $R_{gt}(F)$ = 0.048, $wR_{ref}(F^2)$ = 0.145, T = 298 K.

Source of material

A mixture of MnCl (0.5 mmol, 0.06 g) and 2-ethyl-1*H*-imidazole-4,5-dicarboxylic acid (0.5 mmol, 0.95 g) dissolved in 10 ml H_2O and 5 ml CH_3OH with pH 8 adjusted by NaOH was stirred for half an hour. After filtration, the filtrate was kept at room temperature. Colorless crystals were obtained by the evaporation of the solvate after three weeks.

Experimental details

Checking the data with PLATON [1] as well as checkcif indicate that the crystal is definitely centrosymmetric space group $P\bar{1}$. The disorder is still present when refining the data in the space group $P1$. Carbon and nitrogen bound H atoms were placed at calculated positions and were refined in the riding mode with d(C—H) = 0.93 Å, d(N—H) = 0.86 Å, and with U_{iso}(H) = 1.2 U_{eq}(C,N). H atoms of the water molecule were located in a difference Fourier map and refined with U_{iso}(H) = 1.2 U_{eq}(O). Carboxyl H atoms were located in a difference Fourier map and were included in the refinement in the riding model with a d(O—H) restraint of 0.82(1) Å and U_{iso}(H) = 1.5 U_{eq}. One disordered lattice water molecule is half-occupied and is located close to an inversion center, one H atom of another water molecule is also half-occupied. The O6 shows elongated thermal ellipsoid, so one H atom of the water molecule was dealt with half occupancy and split into two atoms. Initially, the H atoms attached to the O6 atom were located from the difference Fourier maps, then their positions were adjusted to meet the ideal O—H distances and ideal H–O–H angles of water molecules.

Discussion

Imidazole-4,5-dicarboxylic acid (H_3Imda) can be deprotonated to generate three types of anions, namely Imda^{3-}, HImda^{2-} and H_2Imda$^-$, and react with metal ions to form fascinating complexes with different structures and useful properties. As an important derivative of H_3Imda, 2-ethyl-1*H*-imidazole-4,5-dicarboxylate has been rarely explored [2-4]. In previous studies, we have obtained a Ca(II) complex based on 2-ethyl-1*H*-imidazole-4,5-dicarboxylate under hydrothermal conditions [5].

The title compound $[Mn(H_2O)_2(C_7H_7N_2O_4)_2] \cdot 3H_2O$ forms discrete complexes in the crystal structure, consisting of one Mn(II) ion, two mono-deprotonated 2-ethyl-1*H*-imidazole-4,5-dicarboxy anions, two coordinate water molecules and three solvate water molecules. Each Mn(II) ion is six-coordinated in a distorted octahedral environment, formed by two oxygen atoms (O1, O1^i) and two nitrogen atoms (N1, N1^i) from two 2-ethyl-4-carboxylato-5-carboxy-1*H*-imidazole ligands in the equatorial plane and two coordinate water molecules in the apical sites (symmetry code i: 1–x,1–y,1–z). The distances Mn—O are 2.227(2) Å and 2.175(2) Å; d(Mn—N) = 2.247(2) Å. Each 2-ethyl-4-carboxylato-5-carboxy-1*H*-imidazole ligand chelates Mn(II) in a bidentate coordination mode through its imidazole nitrogen atom and carboxylate oxygen atom. The crystal structure is stabilized by extensive hydrogen-bonding interactions (N–H···O and O–H···O). The uncoordinated water showed significantly elongated thermal ellipsoids, indicating that there is a certain degree of disorder. Thus, O7 located close to an inversion center is half-occupied, one H atom of the water molecule was dealt with half occupancy and split into two atoms.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.21 × 0.30 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	7.01 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	49.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2689, 1822
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1518
$N(param)_{refined}$:	152
Programs:	PLATON [1], SHELXS-97, SHELXL-97, SHELXTL [5]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(2)	2*i*		0.8228	0.1846	0.1583	0.037
H(3)	2*i*		0.7675	–0.1605	0.6061	0.069
H(5C)	2*i*		0.8163	0.5549	0.5915	0.061
H(5D)	2*i*		0.8859	0.3802	0.6226	0.061
H(6D)	2*i*		0.8196	0.2344	0.8663	0.085
H(6E)	2*i*	0.50	0.7363	0.1201	0.9755	0.085
H(6F)	2*i*	0.50	0.9359	0.0715	0.9818	0.085
H(7F)	2*i*	0.50	0.5293	0.0910	–0.0808	0.123
H(7G)	2*i*	0.50	0.4760	0.0499	0.0684	0.123
H(6A)	2*i*		0.5587	0.6182	0.0768	0.046
H(6B)	2*i*		0.7043	0.5139	0.0007	0.046
H(7A)	2*i*		0.8145	0.6365	0.2028	0.088
H(7B)	2*i*		0.8390	0.7055	0.0237	0.088
H(7C)	2*i*		0.9674	0.5155	0.1451	0.088

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(1)	1*h*		½	½	½	0.0339(4)	0.0291(4)	0.0325(4)	–0.0008(3)	–0.0022(3)	–0.0220(3)
N(1)	2*i*		0.6399(3)	0.3465(3)	0.3688(3)	0.029(1)	0.025(1)	0.028(1)	–0.001(1)	–0.003(1)	–0.016(1)
N(2)	2*i*		0.7761(4)	0.2039(3)	0.2350(3)	0.032(1)	0.036(1)	0.030(1)	–0.004(1)	0.002(1)	–0.023(1)
O(1)	2*i*		0.5544(3)	0.2202(3)	0.6710(3)	0.050(1)	0.037(1)	0.032(1)	–0.007(1)	0.006(1)	–0.021(1)
O(2)	2*i*		0.6733(4)	–0.0572(3)	0.7112(3)	0.069(2)	0.032(1)	0.034(1)	–0.012(1)	0.005(1)	–0.013(1)
O(3)	2*i*		0.8251(4)	–0.2178(3)	0.5611(3)	0.059(2)	0.028(1)	0.050(2)	–0.006(1)	–0.001(1)	–0.023(1)
O(4)	2*i*		0.9317(4)	–0.1600(3)	0.3287(3)	0.052(1)	0.036(1)	0.054(2)	0.001(1)	–0.001(1)	–0.032(1)
O(5)	2*i*		0.7836(3)	0.4691(3)	0.5985(3)	0.035(1)	0.038(1)	0.085(2)	0.002(1)	–0.013(1)	–0.041(1)
O(6)	2*i*		0.8319(4)	0.1579(4)	0.9614(3)	0.071(2)	0.099(2)	0.051(2)	–0.018(2)	0.010(1)	–0.049(2)
O(7)	2*i*	0.50	0.551(2)	0.011(2)	0.014(2)	0.12(1)	0.110(7)	0.071(6)	–0.044(7)	0.028(7)	–0.034(4)
C(1)	2*i*		0.6341(4)	0.1079(4)	0.6251(3)	0.034(2)	0.035(2)	0.030(2)	–0.008(1)	–0.001(1)	–0.018(1)
C(2)	2*i*		0.6836(4)	0.1684(4)	0.4624(3)	0.027(1)	0.028(2)	0.029(2)	–0.005(1)	–0.004(1)	–0.017(1)
C(3)	2*i*		0.7700(4)	0.0781(4)	0.3804(3)	0.027(2)	0.029(2)	0.034(2)	–0.003(1)	–0.005(1)	–0.020(1)
C(4)	2*i*		0.8487(4)	–0.1131(4)	0.4233(4)	0.033(2)	0.029(2)	0.041(2)	–0.003(1)	–0.008(1)	–0.021(2)
C(5)	2*i*		0.6969(4)	0.3640(4)	0.2310(3)	0.028(2)	0.033(2)	0.029(2)	–0.004(1)	–0.003(1)	–0.019(1)
C(6)	2*i*		0.6867(5)	0.5322(4)	0.0942(4)	0.043(2)	0.039(2)	0.029(2)	–0.010(2)	–0.001(1)	–0.015(1)
C(7)	2*i*		0.8413(6)	0.6041(5)	0.1187(5)	0.068(3)	0.055(2)	0.047(2)	–0.029(2)	–0.006(2)	–0.012(2)

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