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Crystal Structure of Catena(tetraaqua-*μ-trans*-4-hydroxy-*L*-proline-O,O′)manganese(II) Sulfate

R. Mrozek[1], **Z. Rzączyńska**[1,*], and **T. Głowiak**[2]

[1] Faculty of Chemistry, Maria Curie-Skłodowska University, PL-20031 Lublin, Poland
[2] Institute of Chemistry, University of Wrocław, PL-50383 Wrocław, Poland

Summary. A new complex of manganese(II) with *trans*-4-hydroxy-*L*-proline of the formula $[Mn(C_5H_8NO_3) \cdot 4H_2O] \cdot SO_4$ was obtained. The compound was studied by thermal analysis, and the structure was determined by direct X-ray diffraction methods. The compound crystallizes in the triclinic system (space group P1) with $a = 7.478(1)$, $b = 9.297(2)$, $c = 9.814(2)$ Å, $\alpha = 87.38(3)$, $\beta = 67.81(3)$, $\gamma = 84.21(3)°$, $Z = 2$. The Mn(II) ions are six-fold coordinated being surrounded by two carboxyl oxygen atoms and four water molecules (Mn–O = 2.144(2)–2.255(2) Å). The carboxylate group bridges two adjacent Mn(II) ions and links to a polymeric chain. The sulfate anion is anchored exclusively *via* hydrogen bonds.

Keywords. Manganese(II) complexes; *trans*-4-Hydroxy-*L*-proline; Crystal structure.

Kristallstruktur von Catena(tetraaqua-*μ-trans*-4-hydroxy-*L*-prolin-O,O′)mangan(II)-sulfat

Zusammenfassung. Ein neuer Mangan(II)-Komplex mit *trans*-4-Hydroxy-*L*-prolin als Liganden und der Formel $[Mn(C_5H_8NO_3) \cdot 4H_2O] \cdot SO_4$ wurde hergestellt. Die Verbindung wurde mittels thermischer Analyse untersucht, und ihre Struktur wurde durch direkte Röntgenmethoden aufgeklärt. Der Komplex kristallisiert im triklinen System (Raumgruppe P1) mit $a = 7.487(1)$, $b = 9.297(2)$, $c = 9.814(2)$ Å, $\alpha = 87.38(3)$, $\beta = 67.81(3)$, $\gamma = 84.21(1)°$, $Z = 2$. Die Mn(II)-Ionen sind sechsfach koordiniert (zwei Carboxylsauerstoffe, vier Wassermoleküle; Mn–O = 2.144(2)–2.255(2) Å). Die Carboxylatgruppe verbrückt zwei benachbarte Mn(II)-Ionen und ist an eine polymere Kette gebunden. Das Sulfatanion wird ausschließlich *via* Wasserstoffbrückenbindungen fixiert.

Introduction

Manganese is one of the twenty-five ''life elements'' and participates in the formation of a variety of metalloenzymes: superoxide dismutase, pyruvate carboxylase [1, 2], arginase, and enolase [3]. Manganese catalases originating from *Thermus thermophilus* and *Lactobacillus plantarum* protect organisms from oxidative damage [4]. To explore the potential possibilities manganese bonding to proteins, a number of investigations on manganese interactions with simple amino acids have been carried out. Many papers suggest that the preferential active binding site on the amino acid is the carboxyl group [5–8], whereas the amino

nitrogen remains rather uncoordinated. Coordination through the nitrogen atom of the amino acid has been postulated in the manganese complex of *L*-aspartic acid [9] and through the imidazole nitrogen atom of the histidine residue in natural systems such as concanvaline A [1]. This mode of bonding is also proposed for some naturally existing enzymes [3].

The present work reports the crystal structure of the manganese(II) complex of *trans*-4-hydroxy-*L*-proline which occurs in natural biosystems, *e.g.* in collagen [10].

Results and Discussion

The light pink crystals of the title compound have the formula $[Mn(L\text{-}Hyp) \cdot 4H_2O] \cdot SO_4$, where *L-Hyp* is *trans*-4-hydroxy-*L*-proline. The compound is stable up to about 358 K and turns then into an anhydrous form which decomposes to $MnSO_4$ (540–900 K) and Mn_3O_4 ($\approx$ 1200 K). The thermal data are shown in Fig. 1.

The structure of the title compound was determined by X-ray single crystal diffraction (Tables 1–4). A part of the structure is shown in Fig. 2. The compound crystallizes in the acentric triclinic space group P1. The absolute configuration could be unequivocally determined *via* anomalous dispersion effects and is in correspondence with the known configuration of *L*-hydroxyproline. There are two independent Mn(II) ions, *L*-hydroxyproline molecules, and SO_4 groups in the asymmetric unit. The two Mn(II) ions display a moderately distorted octahedral coordination, surrounded by four H_2O molecules and two carboxyl O-atoms in *cis*-configuration. The amino acid molecules exist as zwitterions. They establish bridging links between pairs of adjacent Mn ions with their carboxylate groups to form infinite chains parallel to the *y* axis. The two sulfate ions are embedded between the chains and are anchored in the structure exclusively *via* hydrogen

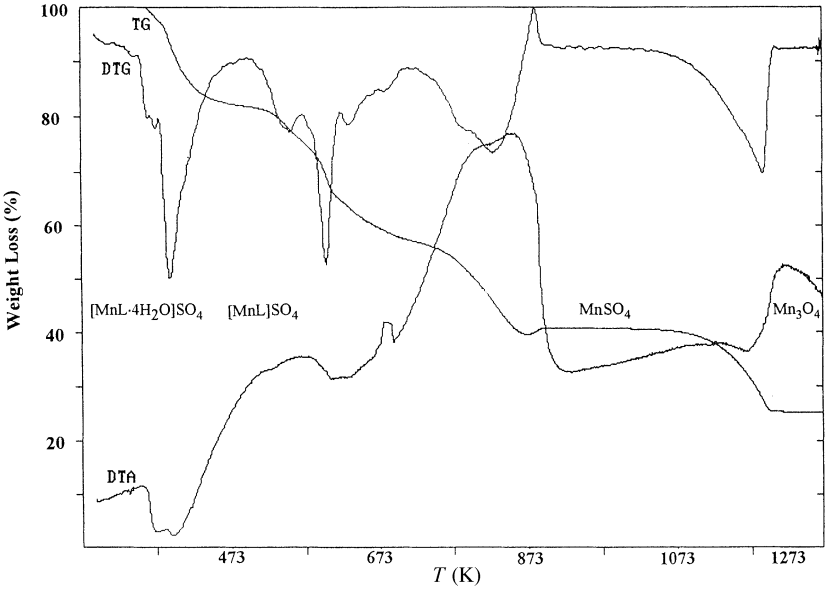

Fig. 1. Thermal decomposition of $[Mn \cdot L\text{-}Hyp \cdot 4H_2O] \cdot SO_4$

Table 1. Crystal data and structure refinement

Formula	$C_5H_{17}MnNO_{11}S$
Color	light pink
M_r	354.20
Crystal system	triclinic
Space group	P1
Temperature (°C)	25
Cell constants (38 reflections, $24.6 < \theta < 38.8°$)	
a (Å)	7.478(1)
b (Å)	9.297(2)
c (Å)	9.814(2)
α (°)	87.38(3)
β (°)	67.81(3)
γ (°)	84.21(3)
Cell volume (Å^3)	628.5(2)
Z	2
$F(000)$	366
D_C (Mg/m^3)	1.872
D_m (flotation, $CCl_4/C_2H_4Br_2$, Mg/m^3)	1.88
μ_{calc} (cm^{-1})	12.72
Diffractometer/scan	Kuma KM4/w $-$ 2θ
Radiation, graphite monochromator	MoKα
Crystal size (mm)	$0.40 \times 0.40 \times 0.40$
Scan width	$1.2 + 0.35 \tan\theta$
No. of standard reflections	3
Decay of standards	$< 3\%$
Reflections measured	2947
2θ range (°)	4.40–55.08
Range of h, k, l	$0 \rightarrow 9,\ -11 \rightarrow 12,\ -11 \rightarrow 12$
Criterion for observed reflections	$I > 3.0\sigma(I)$
No. of observed reflections	2859
Corrections applied	extinction, *Lorentz*, polarization
Computer programs	SHELXS-86, SHELXL-93
Structure solution	direct method
No. of parameters varied	110
Weights[a] (a, b, f)	0.0476, 0.0854, 1/3
GOF	1.099
$R_1 = \sum(\lvert F_o\rvert - \lvert F_c\rvert)/\sum(\lvert F_o\rvert)$	0.0231
$wR_2 = (\sum(wF_o^2 = F_o^2)^2/\sum(w(F_o^2)^2))^{1/2}$	0.0613
Function minimized	$\sum w(\Delta F^2)^2$
Flack's absolute structure parameter	0.008(11)
Extinction coefficient	0.391(10)
Largest diff. peak and hole (e · Å^{-3})	0.473 and $-$0.491

[a] $w = 1/(\sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P)$ where $P = (f \cdot \text{Max of } (0 \text{ or } F_o^2) + (1 - f) \cdot F_c^2)$

bonds. The Mn–$O_{carboxyl}$ distances fall in the range of 2.144(2)–2.255(2) Å, and Mn–O_{water} bonds are in the region of 2.141(3)–2.255(2) Å. These values are in good agreement with data found earlier for the complex of Mn(II) with *DL*-proline [7] and *L*-proline [8]. The O–C–O angles in *L*-hydroxyproline are about 126°

Table 2. Final atomic coordinates and equivalent isotropic thermal parameters (Å^2) for non-hydrogen atoms with esd values in parentheses

	x	y	z	U_{eq}
Mn(1)	0.4000	0.2000	0.2000	0.01880(11)
Mn(2)	0.24588(7)	0.69673(5)	0.55592(6)	0.01860(11)
S(1)	0.54788(10)	− 0.25101(8)	− 0.08696(8)	0.01996(15)
S(2)	0.08227(10)	0.23455(7)	− 0.16648(8)	0.01798(14)
O(1)	0.7011(3)	− 0.1928(3)	− 0.0528(2)	0.0269(4)
O(2)	0.4683(4)	− 0.3706(3)	0.0125(3)	0.0457(7)
O(3)	0.3914(4)	− 0.1358(3)	− 0.0717(3)	0.0420(6)
O(4)	0.6286(3)	− 0.2994(3)	− 0.2412(3)	0.0357(5)
O(5)	− 0.0106(3)	0.2045(3)	− 0.0062(2)	0.0258(4)
O(6)	− 0.0492(4)	0.3371(3)	− 0.2099(3)	0.0335(5)
O(7)	0.1230(3)	0.1008(2)	− 0.2496(3)	0.0316(5)
O(8)	0.2674(3)	0.2985(2)	− 0.1937(2)	0.0257(4)
O(9)	0.5727(3)	0.3480(2)	0.2447(3)	0.0253(4)
O(10)	0.3948(3)	0.5407(2)	0.3689(2)	0.0247(4)
O(11)	1.0931(3)	0.6847(3)	0.2027(2)	0.0293(5)
O(12)	0.4281(3)	0.8732(2)	0.5257(2)	0.0217(4)
O(13)	0.3685(3)	1.0429(2)	0.3769(2)	0.0254(4)
O(14)	0.8252(3)	1.2790(2)	0.5628(3)	0.0296(5)
O(15)	0.1467(3)	0.3536(2)	0.3327(2)	0.0256(4)
O(16)	0.2210(3)	0.0704(2)	0.1329(3)	0.0289(4)
O(17)	0.4061(5)	0.3462(3)	0.0189(3)	0.0483(7)
O(18)	0.6592(3)	0.0699(3)	0.0757(3)	0.0447(7)
O(19)	0.4090(4)	0.5598(3)	0.6587(3)	0.0357(5)
O(20)	0.0756(3)	0.8126(3)	0.7585(3)	0.0349(5)
O(21)	− 0.0025(3)	0.5707(2)	0.6165(3)	0.0289(4)
O(22)	0.1246(3)	0.8248(2)	0.4182(3)	0.0275(4)
N(1)	0.9075(3)	0.4578(2)	0.1685(3)	0.0203(4)
N(2)	0.5366(3)	1.0561(3)	0.6732(3)	0.0240(5)
C(1)	0.5516(4)	0.4698(3)	0.3025(3)	0.0175(4)
C(2)	0.7400(4)	0.5284(3)	0.2935(3)	0.0190(5)
C(3)	0.7524(4)	0.6917(3)	0.2624(4)	0.0257(6)
C(4)	0.9498(4)	0.7023(3)	0.1390(3)	0.0229(5)
C(5)	0.9698(4)	0.5693(3)	0.0493(3)	0.0234(5)
C(7)	0.5453(4)	1.0997(3)	0.5217(3)	0.0168(4)
C(6)	0.4371(3)	0.9973(3)	0.4710(3)	0.0160(4)
C(9)	0.8518(4)	1.1263(3)	0.5393(3)	0.0222(5)
C(8)	0.7626(4)	1.0943(3)	0.4289(3)	0.0223(5)
C(10)	0.7368(5)	1.0452(4)	0.6742(4)	0.0315(6)

Final H-atom coordinates and isotropic thermal parameters (Å^2)

	x	y	z	U_{iso}
H(11H)	1.2000(10)	0.666(6)	0.1380(8)	0.044
H(14H)	0.850(7)	1.2965(5)	0.635(3)	0.044
H(1A)	1.0056(3)	0.4274(2)	0.1978(3)	0.024
H(1B)	0.8710(3)	0.3811(2)	0.1360(3)	0.024
H(2A)	0.4597(3)	1.1222(3)	0.7390(3)	0.029

Table 2 (continued)

	x	y	z	U_{iso}
H(2B)	0.4865(3)	0.9703(3)	0.6983(3)	0.029
H(2C)	0.7596(4)	0.5053(3)	0.3856(3)	0.023
H(3A)	0.6489(4)	0.7324(3)	0.2315(4)	0.031
H(3B)	0.7441(4)	0.7422(3)	0.3492(4)	0.031
H(4C)	0.9561(4)	0.7920(3)	0.0815(3)	0.027
H(5A)	0.8853(4)	0.5803(3)	− 0.0057(3)	0.028
H(5B)	1.1026(4)	0.5467(3)	− 0.0178(3)	0.028
H(7C)	0.4859(4)	1.1988(3)	0.5234(3)	0.020
H(9C)	0.9895(4)	1.0912(3)	0.5041(3)	0.027
H(8A)	0.8118(4)	0.9997(3)	0.3856(3)	0.027
H(8B)	0.7894(4)	1.1666(3)	0.3511(3)	0.027
H(10A)	0.7893(5)	0.9450(4)	0.6701(4)	0.038
H(10B)	0.7370(5)	1.0887(4)	0.7621(4)	0.038
H(1)	0.2008	0.4185	0.3690	0.050
H(2)	0.0694	0.3420	0.4089	0.050
H(3)	0.2510	− 0.0009	0.0891	0.050
H(4)	0.1334	0.0954	0.1089	0.050
H(5)	0.3600	0.3288	− 0.0511	0.050
H(6)	0.4323	0.4385	0.0170	0.050
H(7)	0.7675	0.0940	0.0483	0.050
H(8)	0.6517	− 0.0113	0.0471	0.050
H(9)	0.4886	0.5987	0.7071	0.050
H(10)	0.3613	0.4725	0.7080	0.050
H(11)	− 0.0383	0.8062	0.8087	0.050
H(12)	0.1260	0.8198	0.8089	0.050
H(13)	− 0.1291	0.6051	0.6286	0.050
H(14)	− 0.0048	0.5012	0.6888	0.050
H(15)	0.1120	0.7795	0.3528	0.050
H(16)	0.2024	0.8894	0.3989	0.050

$U_{eq} = \frac{1}{3}\sum_{ij} U_{ij} a_i^* a_j^* \bar{a}_i \bar{a}_j$

which is characteristic for bridging bidentate carboxylate groups. The C–O bonds lengths in the carboxylate groups are in the range of 1.241(3)–1.259(4) Å. Both carboxyl groups link Mn(II) ions in a *syn-anti* type of configuration.

The *L*-hydroxyproline rings have twisted conformations about the C4–C5 and C8–C9 bonds, with these atoms deviating by 0.286(7) and − 0.435(6) Å from the C2–C3–N1 plane of one *L-Hyp* molecule and − 0.188(8) and 0.431(8) Å from the C7–C10–N2 plane of the second *L-Hyp* ring. The carboxylate groups O9–C1–O10 and O12–C6–O13 are rotated by 50.2(2)° and 62.8(2)° from the C2–C3–N1 and C7–C10–N2 plane of the proline ring, respectively. The C–O–Mn angles are in the range of 136.6(2)–143.6(2)°. The C–C and C–N bond lengths are within normal ranges.

The compound exhibits a complicated system of hydrogen bonds. Corresponding distances and angles are presented in Table 4. Each of the water molecules donates two O–H···O bonds (except of O20). The O···O separations are between

Table 2a. Anisotropic displacement parameters (Å^2) for non-hydrogen atoms with esd values in parentheses

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn(1)	0.0221(2)	0.0158(2)	0.0207(2)	0.00077(13)	− 0.0105(2)	− 0.00366(13)
Mn(2)	0.0190(2)	0.0152(2)	0.0218(2)	− 0.00045(13)	− 0.0076(2)	− 0.00229(13)
S(1)	0.0189(3)	0.0179(3)	0.0216(3)	0.0000(2)	− 0.0052(2)	− 0.0046(2)
S(2)	0.0192(3)	0.0161(3)	0.0197(3)	− 0.0027(2)	− 0.0081(2)	− 0.0024(2)
O(1)	0.0237(9)	0.0315(10)	0.0284(10)	− 0.0038(8)	− 0.0122(8)	− 0.0046(8)
O(2)	0.059(2)	0.0277(12)	0.0431(14)	0.0098(10)	− 0.0085(13)	− 0.0186(11)
O(3)	0.0301(11)	0.0391(13)	0.057(2)	− 0.0119(12)	− 0.0185(11)	0.0115(10)
O(4)	0.0277(10)	0.0529(15)	0.0251(11)	− 0.0116(10)	− 0.0067(9)	− 0.0054(10)
O(5)	0.0237(9)	0.0315(11)	0.0207(9)	0.0003(8)	− 0.0062(8)	− 0.0051(8)
O(6)	0.0349(11)	0.0283(11)	0.0423(13)	0.0067(9)	− 0.0214(10)	− 0.0008(9)
O(7)	0.0342(11)	0.0220(10)	0.0353(12)	− 0.0138(9)	− 0.0070(9)	− 0.0055(8)
O(8)	0.0240(9)	0.0266(10)	0.0276(10)	− 0.0010(8)	− 0.0089(8)	− 0.0103(8)
O(9)	0.0219(9)	0.0200(9)	0.0348(11)	− 0.0067(8)	− 0.0105(8)	− 0.0027(7)
O(10)	0.0181(8)	0.0266(10)	0.0269(9)	− 0.0085(7)	− 0.0049(7)	− 0.0012(7)
O(11)	0.0204(9)	0.0391(12)	0.0287(10)	− 0.0064(9)	− 0.0072(8)	− 0.0093(8)
O(12)	0.0242(9)	0.0177(9)	0.0266(10)	0.0029(7)	− 0.0129(8)	− 0.0055(7)
O(13)	0.0317(10)	0.0255(9)	0.0256(9)	0.0081(7)	− 0.0172(8)	− 0.0106(8)
O(14)	0.0376(12)	0.0210(10)	0.0348(11)	− 0.0009(8)	− 0.0173(10)	− 0.0094(9)
O(15)	0.0220(9)	0.0226(10)	0.0308(10)	− 0.0010(8)	− 0.0076(8)	− 0.0042(7)
O(16)	0.0318(11)	0.0249(10)	0.0378(11)	− 0.0041(8)	− 0.0214(9)	− 0.0017(8)
O(17)	0.091(2)	0.0318(12)	0.0462(15)	0.0184(11)	− 0.049(2)	− 0.0312(14)
O(18)	0.0268(11)	0.0321(13)	0.061(2)	− 0.0191(12)	0.0041(11)	− 0.0099(9)
O(19)	0.0481(13)	0.0260(10)	0.0462(13)	0.0052(9)	− 0.0332(12)	− 0.0044(9)
O(20)	0.0293(10)	0.0361(12)	0.0310(11)	− 0.0103(9)	0.0008(9)	− 0.0100(9)
O(21)	0.0235(9)	0.0235(10)	0.0374(12)	0.0014(8)	− 0.0080(9)	− 0.0069(8)
O(22)	0.0365(11)	0.0210(9)	0.0327(11)	− 0.0002(8)	− 0.0211(9)	− 0.0047(8)
N(1)	0.0183(10)	0.0160(9)	0.0263(11)	− 0.0051(8)	− 0.0082(8)	0.0005(8)
N(2)	0.0219(11)	0.0343(13)	0.0176(10)	0.0026(9)	− 0.0080(9)	− 0.0088(9)
C(1)	0.0180(10)	0.0185(11)	0.0162(10)	0.0002(8)	− 0.0067(8)	− 0.0020(9)
C(2)	0.0170(11)	0.0196(12)	0.0201(11)	− 0.0060(9)	− 0.0065(9)	− 0.0003(9)
C(3)	0.0197(12)	0.0166(12)	0.0363(15)	− 0.0091(10)	− 0.0051(11)	0.0001(9)
C(4)	0.0235(12)	0.0193(12)	0.0252(13)	− 0.0035(10)	− 0.0074(10)	− 0.0044(9)
C(5)	0.0283(13)	0.0224(13)	0.0201(11)	− 0.0039(10)	− 0.0094(10)	− 0.0015(10)
C(7)	0.0169(10)	0.0177(11)	0.0166(10)	0.0000(8)	− 0.0071(8)	− 0.0023(8)
C(6)	0.0134(9)	0.0168(11)	0.0175(10)	0.0000(8)	− 0.0053(8)	− 0.0027(8)
C(9)	0.0202(11)	0.0194(12)	0.0289(13)	0.0010(10)	− 0.0108(10)	− 0.0050(9)
C(8)	0.0184(11)	0.0254(13)	0.0225(12)	− 0.0019(9)	− 0.0057(9)	− 0.0063(9)
C(10)	0.0292(13)	0.035(2)	0.038(2)	0.0167(12)	− 0.0215(12)	− 0.0104(12)

The anisotropic displacement factor exponent can be expressed as $-2\pi^2(h^2a^2 \cdot U_{11} + \cdots + 2\,h \cdot k \cdot a \cdot b \cdot U_{12})$

2.629(5) and 2.856(4) Å. The hydroxyl oxygens of *L-Hyp* participate in intermolecular hydrogen bonds. The protonated NH_2^+ group of *L*-hydroxyproline is a donor of protons for three hydrogen bonds, one of them (N–H1B···O9) being intraligand. This contact is considerably shorter compared to other observed

Table 3. Selected bond lengths (Å) and bond angles (°)

Mn(1)–O(18)		2.141(3)	Mn(2)–O(19)		2.150(2)
Mn(1)–O(9)		2.144(2)	Mn(2)–O(22)		2.152(2)
Mn(1)–O(13)^{i}		2.176(2)	Mn(2)–O(21)		2.172(2)
Mn(1)–O(17)		2.177(2)	Mn(2)–O(12)		2.177(2)
Mn(1)–O(16)		2.177(2)	Mn(2)–O(20)		2.178(2)
Mn(1)–O(15)		2.255(2)	Mn(2)–O(10)		2.255(2)
S(1)–O(1)	1.466(2)		S(2)–O(5)	1.486(2)	
S(1)–O(2)	1.462(2)		S(2)–O(6)	1.465(2)	
S(3)–O(3)	1.473(2)		S(2)–O(7)	1.460(2)	
S(4)–O(4)	1.475(2)		S(2)–O(8)	1.488(2)	
O(9)–C(1)	1.259(3)		O(13)–C(6)	1.254(3)	
O(10)–C(1)	1.241(3)		O(12)–C(6)	1.247(3)	
O(9)–C(1)–O(10)		126.0(2)	O(12)–C(6)–O(13)		125.8(2)
O-Mn(1)–O	83.6(1)–101.0(1)		O–Mn(2)–O	81.7(1)–108.1(1)	
O–Mn(1)–O	172.4(1)–174.2(1)		O–Mn(2)–O	163.1(1)–170.1(1)	

^{i} Symmetry code: $x, y - 1, z$

Table 4. Hydrogen bond lengths (Å) and angles (°)

D–H···A	D–H	H···A	D···A	D–H···A
O(11)-H(11H)···O(2)^{i}	0.82	1.92	2.731(4)	170
O(14)-H(14H)···O(6)^{ii}	0.82	2.00	2.819(4)	171
O(15)-H(1)···O(10)	0.91	1.93	2.793(4)	157
O(15)-H(2)···O(14)^{iii}	0.76	2.00	2.730(5)	159
O(16)-H(3)···O(3)	0.77	1.96	2.694(4)	159
O(16)-H(4)···O(5)	0.79	2.01	2.759(4)	158
O(17)-H(5)···O(8)	0.91	1.82	2.728(4)	179
O(17)-H(6)···O(2)^{iv}	0.90	1.82	2.713(4)	176
O(18)-H(7)···O(5)^{v}	0.80	1.93	2.710(4)	164
O(18)-H(8)···O(1)	0.83	1.92	2.735(4)	165
O(19)-H(9)···O(4)^{vi}	0.99	1.70	2.674(4)	165
O(19)-H(10)···O(8)^{vii}	0.96	1.90	2.856(4)	180
O(2)-H(11)···O(1)^{viii}	0.81	1.91	2.716(4)	172
O(21)-H(13)···O(4)^{viii}	0.93	1.93	2.755(4)	146
O(21)-H(14)···O(6)^{vii}	0.93	1.77	2.666(4)	159
O(22)-H(15)···O(11)^{ix}	0.82	1.81	2.629(5)	177
O(22)-H(16)···O(13)	0.84	1.94	2.778(5)	174
N(1)-H(1A)···O(15)^{v}	0.90	2.04	2.904(5)	160
N(1)-H(1B)···O(5)^{v}	0.90	2.10	2.855(4)	140
N(1)-H(1B)···O(9)	0.90	2.13	2.628(4)	114
N(2)-H(2A)···O(8)^{vi}	0.90	2.02	2.864(4)	155
N(2)-H(2B)···O(12)	0.90	2.16	2.652(4)	114
N(2)-H(2B)···O(3)^{vi}	0.90	2.30	2.926(4)	126

Symmetry code: (i) $1 + x, 1 + y, z$; (ii) $1 + x, 1 + y, 1 + z$; (iii) $1 - x, 1 - y, z$; (iv) $x, 1 + y, z$; (v) $1 + x, y, z$; (vi) $x, 1 + y, 1 + z$; (vii) $x, y, 1 + z$; (viii) $1 - x, 1 + y, 1 + z$; (ix) $1 - x, y, z$

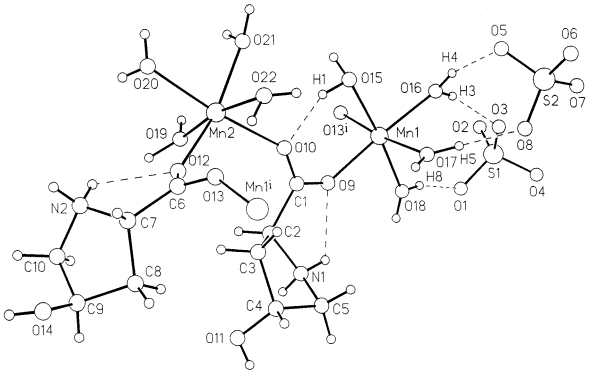

Fig. 2. View of the crystal structure of catena(tetraaqua-*trans*-μ-4-hydroxy-*L*-proline-O,O′)manganese(II) sulfate

hydrogen bonds. Each sulfate group is connected with the rest of the structure *via* two O–H···O hydrogen bonds per sulfate oxygen.

Experimental

Crystals of catena(tetraaqua-μ-*trans*-4-hydroxy-*L*-proline-O,O′)manganese(II) sulfate were grown by slow evaporation of an aqueous solution of *trans*-4-hydroxy-*L*-proline and manganese(II) sulfate in a molar ratio of 1:2. Light pink crystals, readily soluble in water, were formed after a few days. $MnSO_4 \cdot 5H_2O$ (analytically pure, 'POCH' Gliwice, Poland) and *trans*-4-hydroxy-*L*-proline (98%, Reanal, Budapest, Hungary) were used.

Thermal analysis of the complex was carried out using a Q 1500 D Paulik-Paulik-Erday derivatograph. A sample of 100 mg was heated to 1273 K in a ceramic crucible at a rate of 10°/min under air. Al_2O_3 was used as a reference material (Fig. 1).

An intermediate decomposition product of red-brown colour was identified as $MnSO_4$ on the basis of the SO_4^{2-} content in $BaSO_4$. The final product of decomposition was identified as Mn_3O_4 from the TG curve and a X-ray the powder diffractogram [13].

The *Weissenberg* photographs afforded the crystal system and the approximate unit cell dimensions. The crystal used had the following approximate dimensions: $0.40 \times 0.40 \times 0.40$ mm. The intensity data were collected on a Kuma KM-4 computer controlled κ-axis diffractometer with graphite monochromated MoKα radiation at room temperature. The stability of intensities was monitored by the measurement of three standards every 100 reflections. The crystallographic data and the refinement procedures are given in Table 1. The intensities were corrected for *Lorentz* and polarization effects, but not for absorption. The structure was solved by direct methods using SHELXS-86 [14] and refined by full matrix least-squares using the SHELXL-93 [15] program. The hydrogen atoms of the water molecules were located from a difference *Fourier* map. Other hydrogen atoms were placed in the geometrically calculated positions with isotropic temperature factors taken as $1.2 \cdot U_{eq}$ of the neighbouring heavier atoms. Scattering factors were those incorporated in SHELXL-93. The final parameters and their estimated standard deviations are listed in Table 2.

References

[1] Siegel H, Fisher BE, Prijs B (1977) J Am Chem Soc **99**: 4489
[2] Frieden E (1985) J Chem Educ **62**: 916
[3] Dismukes GC (1996) Chem Rev **96**: 2909
[4] Holm RH, Kennepohl P, Solomon EJ (1996) Chem Rev **96**: 2239
[5] Ciunik Z, Głowiak T (1980) Acta Cryst **B36**: 1212

[6] Clegg W, Oi Mi Lacy, Straughan BP (1987) Acta Cryst **C43**: 794
[7] Głowiak T, Ciunik Z (1977) Acta Cryst **B33**: 3237
[8] Rzączyńska Z, Mrozek R, Głowiak T (1997) J Chem Crystallogr **27**(7): 417
[9] Schmidbaur H, Bach I, Riede J, Muller G, Helbig J, Hopf G (1988) Chem Ber **121**: 795
[10] Harper AH, Rodwell WR, Mayes PA (1979) Review of Physiological Chemistry. Los Altos, California, p 545
[11] Alcock NW, Tracy VM, Waddington TC (1976) J Chem Soc Dalton Trans **19**: 2243
[12] Nakamoto K (1976) Infrared and Raman Spectra of Inorganic and Coordination Compounds. Wiley, New York, p 231
[13] Powder Diffraction Data (1976) Joint Committee on Powder Diffraction Standards, Park Lane, Swarthmore, Pennsylvania, p 386
[14] Sheldrick GM (1990) Acta Cryst **A46**: 467
[15] Sheldrick GM SHELXL 93 (1994) Program for Refinement of Crystal Structures. University of Göttingen, Germany.

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