

UDC 541.49;548.737

**CRYSTAL STRUCTURES OF SEVEN-COORDINATE  $(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{edta})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{cydta})(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$  AND  $\text{K}_2[\text{Mn}^{\text{II}}(\text{Hdtpa})] \cdot 3.5\text{H}_2\text{O}$  COMPLEXES**© 2008 X.F. Wang<sup>1</sup>, J. Gao<sup>2</sup>, J. Wang<sup>1,2\*</sup>, Zh.H. Zhang<sup>3</sup>, Y.F. Wang<sup>2</sup>, L.J. Chen<sup>1</sup>, W. Sun<sup>2</sup>, X.D. Zhang<sup>2</sup><sup>1</sup>Department of Pharmacy, Liaoning University, Shenyang, 110036, P.R. China;<sup>2</sup>Department of Chemistry, Liaoning University, Shenyang, 110036, P.R. China;<sup>3</sup>Department of Environment, Liaoning University, Shenyang, 110036, P.R. China

Received August, 4, 2007

The title compounds,  $(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{edta})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$  ( $\text{H}_4\text{edta}$  = ethylenediamine-*N,N,N',N'*-tetraacetic acid),  $(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{cydta})(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$  ( $\text{H}_4\text{cydta}$  = *trans*-1,2-cyclohexanediamine-*N,N,N',N'*-tetraacetic acid) and  $\text{K}_2[\text{Mn}^{\text{II}}(\text{Hdtpa})] \cdot 3.5\text{H}_2\text{O}$  ( $\text{H}_5\text{dtpa}$  = diethylenetriamine-*N,N,N',N'',N''*-pentaacetic acid), were prepared; their compositions and structures were determined by elemental analysis and single-crystal X-ray diffraction technique. In these three complexes, the  $\text{Mn}^{2+}$  ions are all seven-coordinated and have a pseudo-monocapped trigonal prismatic configuration. All the three complexes crystallize in triclinic system in *P*-1 space group. Crystal data:  $(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{edta})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$  complex,  $a = 8.774(3) \text{ \AA}$ ,  $b = 9.007(3) \text{ \AA}$ ,  $c = 13.483(4) \text{ \AA}$ ,  $\alpha = 80.095(4)^\circ$ ,  $\beta = 80.708(4)^\circ$ ,  $\gamma = 68.770(4)^\circ$ ,  $V = 972.6(5) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.541 \text{ g/cm}^3$ ,  $\mu = 0.745 \text{ mm}^{-1}$ ,  $R = 0.033$  and  $wR = 0.099$  for 3406 observed reflections with  $I \geq 2\sigma(I)$ ;  $(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{cydta})(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$  complex,  $a = 8.9720(18) \text{ \AA}$ ,  $b = 9.4380(19) \text{ \AA}$ ,  $c = 14.931(3) \text{ \AA}$ ,  $\alpha = 76.99(3)^\circ$ ,  $\beta = 83.27(3)^\circ$ ,  $\gamma = 75.62(3)^\circ$ ,  $V = 1190.8(4) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.426 \text{ g/cm}^3$ ,  $\mu = 0.625 \text{ mm}^{-1}$ ,  $R = 0.061$  and  $wR = 0.197$  for 3240 observed reflections with  $I \geq 2\sigma(I)$ ;  $\text{K}_2[\text{Mn}^{\text{II}}(\text{Hdtpa})] \cdot 3.5\text{H}_2\text{O}$  complex,  $a = 8.672(3) \text{ \AA}$ ,  $b = 9.059(3) \text{ \AA}$ ,  $c = 15.074(6) \text{ \AA}$ ,  $\alpha = 95.813(6)^\circ$ ,  $\beta = 96.665(6)^\circ$ ,  $\gamma = 99.212(6)^\circ$ ,  $V = 1152.4(7) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.687 \text{ g/cm}^3$ ,  $\mu = 1.006 \text{ mm}^{-1}$ ,  $R = 0.037$  and  $wR = 0.090$  for 4654 observed reflections with  $I \geq 2\sigma(I)$ .

**Keywords:** manganese(II) chelate, ethylenediamine-*N,N,N',N'*-tetraacetic acid ( $\text{H}_4\text{edta}$ ), *trans*-1,2-cyclohexanediamine-*N,N,N',N'*-tetraacetic acid ( $\text{H}_4\text{cydta}$ ), diethylenetriamine-*N,N,N',N'',N''*-pentaacetic acid ( $\text{H}_5\text{dtpa}$ ).

**INTRODUCTION**

The  $\text{Mn}^{2+}$  is a transition metal ion with five unpaired electrons; it exhibits strong paramagnetism and can effectively shorten  $T_1$  relaxation time. Hence, some  $\text{Mn}^{2+}$  complexes are used as liver-specific contrast agents. Although they are safer than other magnetic resonance imaging (MRI) contrast agents [1–4], the superfluous free  $\text{Mn}^{2+}$  ions are poisonous for a patient's body. Consequently, the removal of the superfluous  $\text{Mn}^{2+}$  ions from the body is an important problem. As suitable excretive medications, the aminopolycarboxylic acid ligands, such as edta ( $\text{H}_4\text{edta}$  = ethylenediaminetetraacetic acid), could combine with various poisonous metal ions to effectively decrease their amount in a patient's body. If the  $\text{Mn}^{2+}$  ion can be coordinated by these aminopolycarboxylic acid ligands yielding stable and soluble complexes, it can be excreted efficiently from a patient's body. A related ligand, cydta ( $\text{H}_4\text{cydta}$  = *trans*-1,2-cyclohexanediamine-*N,N,N',N'*-tetraacetic acid) is also a hexadentate chelating agent; the ligand possesses certain rigidity due to the cyclohexane group. Various metal ions with ap-

\* E-mail: wangjun890@126.com; wangjuncomplex890@126.com

appropriate ionic radii and electronic configurations can yield stable and soluble complexes with the edta and cydta ligands [ 5—14 ]. However, as the hexadentate edta or cydta ligands provide only six donor atoms while coordinating the  $\text{Mn}^{2+}$  ion, the remainder coordination site on the  $\text{Mn}^{2+}$  ion may be occupied by a water molecule. The dtpa ( $\text{H}_5\text{dtpa}$  = diethylenetriamine- $\text{N,N,N',N'',N''}$ -pentaacetic acid) is another aminopolycarboxylic acid ligand [ 15 ] which is octadentate. When the dtpa ligand coordinates to the  $\text{Mn}^{2+}$  ion, it provides seven donor atoms also to produce a seven-coordinate complex. The non-coordinated carboxyl group ( $-\text{COOH}$ ) of the ligand can be modified to create functions of biological importance [ 16 ]. The three title complexes with edta, cydta and dtpa ligands have been isolated and studied in this work; they all adopt seven-coordinate structure with a pseudo-monocapped trigonal prism configuration. The reported results may provide valuable information for the development of biomedical applications of  $\text{Mn}^{2+}$  complexes.

## EXPERIMENTAL

### *Syntheses of the Complexes*

**$(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{edta})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ .**  $\text{H}_4\text{edta}$  (1.461 g, 5.0 mmol) was added to water (100 ml); then  $\text{MnCO}_3$  powder (0.575 g, 5.0 mmol) was added to the solution slowly. After the mixture was continuously stirred and refluxed for 14 h, it turned into a transparent solution. After that, the pH value of the solution was adjusted with aqueous  $\text{NH}_3$  to  $\sim 6.5$ . The solution was concentrated to 25 ml and left to evaporate slowly at room temperature. Light yellow crystals of the compound were obtained after about two weeks. Anal. Found (%): C 26.64, H 6.24, N 12.44; Calc. (%): C 26.61, H 6.25, N 12.42.

**$(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{cydta})(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$ .** Following the above procedure but using  $\text{H}_4\text{cydta}$  (1.732 g, 5.0 mmol), light yellow crystals of the compound were prepared. Anal. Found (%): C 32.14, H 6.90, N 10.72; Calc. (%): C 32.07, H 6.87, N 10.69.

**$\text{K}_2[\text{Mn}^{\text{II}}(\text{Hdtpa})] \cdot 3.5\text{H}_2\text{O}$ .**  $\text{H}_5\text{dtpa}$  (1.967 g, 5.0 mmol) was added to water (100 ml); then  $\text{MnCO}_3$  powder (0.575 g, 5.0 mmol) was added to the solution slowly. After the mixture was continuously stirred and refluxed for 15 h, it turned into a transparent solution. After that, the pH value of the solution was adjusted with aqueous  $\text{KHCO}_3$  to  $\sim 6$ . The solution was concentrated to 25 ml and left to evaporate slowly at room temperature. Light yellow crystals of the compound were obtained after about two weeks. Anal. Found (%): C 28.74, H 4.50, N 7.20; Calc. (%): C 28.72, H 4.48, N 7.18.

The elemental analyses for C, H and N were carried out on a Perkin-Elmer 240 elemental analysis instrument.

### *X-Ray Structure Determination*

X-ray intensity data were collected on a Bruker SMART CCD X-ray diffractometer with graphite-monochromatized  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.071073$  nm). The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method. All the calculations were performed using SHELXTL-97 on PDP11/44 and Pentium MMX/166 computers [ 17 ]. The crystal data and structure refinement parameters for these three complexes are listed in Table 1. Selected bond lengths and angles are listed in Tables 2—4.

## RESULTS AND DISCUSSION

**$(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{edta})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ .** As shown in Fig. 1, the central  $\text{Mn}^{2+}$  ion in the compound is seven-coordinated by one edta ligand and a water molecule. The seven donor atoms, including four carboxyl oxygen atoms and two amine nitrogen atoms, which come from the same edta ligand, and an oxygen atom from the water molecule, yield a pseudo-monocapped trigonal prismatic configuration. As shown in Fig. 2, the set of N1, O1 and O3 atoms and the set of N2, O5 and O7 atoms form two approximately parallel triangle faces. The seventh donor atom O9 from the water molecule acts as a cap and lies above the plane formed by O1, O3, O7 and O5. The average Mn—O bond distance is 2.2420(18) Å, with the longest one being 2.3017(17) Å (Mn—O7), and the shortest one being 2.1809(17) Å (Mn—O3). The Mn—N bond distances are longer than Mn—O. The Mn—N1 and Mn—N2 bond distances are 2.3682(19) Å and 2.3628(19) Å, respectively. As a hexadentate ligand,

Table 1

## Crystal Data and Structure Refinement for the Compounds Studied

Compound	$(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{edta})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$	$(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{cydta})(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$	$\text{K}_2[\text{Mn}^{\text{II}}(\text{Hdtpa})] \cdot 3.5\text{H}_2\text{O}$
Empirical formula	$\text{C}_{10}\text{H}_{28}\text{MnN}_4\text{O}_{12}$	$\text{C}_{14}\text{H}_{36}\text{MnN}_4\text{O}_{13}$	$\text{C}_{14}\text{H}_{26}\text{MnN}_3\text{O}_{13.50}\text{K}_2$
Formula weight	451.30	523.78	585.52
Temperature, K	294(2)	293(2)	293(2)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
Unit cell dimensions			
<i>a</i> , Å	8.774(3)	8.9720(18)	8.672(3)
<i>b</i> , Å	9.007(3)	9.4380(19)	9.059(3)
<i>c</i> , Å	13.483(4)	14.931(3)	15.074(6)
α, deg.	80.095(4)	76.99(3)	95.813(6)
β, deg.	80.708(4)	83.27(3)	96.665(6)
γ, deg.	68.770(4)	75.62(3)	99.212(6)
<i>V</i> , Å <sup>3</sup>	972.6(5)	1190.8(4)	1152.4(7)
<i>Z</i>	2	2	2
Calculated density, g·cm <sup>-3</sup>	1.541	1.461	1.687
Crystal size, mm	0.20 × 0.20 × 0.16	0.25 × 0.21 × 0.18	0.24 × 0.22 × 0.16
θ range, deg.	1.54 to 25.01	1.40 to 25.08	2.29 to 26.39
Completeness to θ <sub>max</sub> , %	99.2	99.9	99.4
Reflections collected	4983	4247	6659
Independent reflections [ <i>R</i> (int)]	3406 [0.0141]	3240 [0.0519]	4654 [0.0221]
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.098	1.043	1.026
Final <i>R</i> <sub>1</sub> and <i>wR</i> <sub>2</sub> indices [ <i>I</i> > 2σ( <i>I</i> )]	0.0333 and 0.0987	0.0608 and 0.1971	0.0368 and 0.0898
Final <i>R</i> <sub>1</sub> and <i>wR</i> <sub>2</sub> indices (all data)	0.0412 and 0.1053	0.0893 and 0.2317	0.0546 and 0.0978
Max peak and hole, e <sup>-</sup> ·Å <sup>-3</sup>	0.49 and -0.36	0.83 and -0.45	0.51 and -0.50
CCDC deposition No.	635765	635766	635767

Table 2

Selected Bond Lengths (Å) and Angles (deg.) in  $(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{edta})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ 

Bond distances (Å)					
Mn(1)—O(1)	2.2366(16)	Mn(1)—O(7)	2.3017(17)	Mn(1)—N(2)	2.3628(19)
Mn(1)—O(3)	2.1809(17)	Mn(1)—O(9)	2.2408(17)		
Mn—O(5)	2.2501(17)	Mn—N(1)	2.3682(19)		
Bond angles (deg.)					
O(1)—Mn(1)—O(3)	101.62(6)	O(3)—Mn(1)—O(7)	82.95(6)	O(5)—Mn(1)—N(2)	72.35(7)
O(1)—Mn(1)—O(5)	82.99(6)	O(3)—Mn(1)—O(9)	96.71(7)	O(7)—Mn(1)—O(9)	74.08(6)
O(1)—Mn(1)—O(7)	154.32(6)	O(3)—Mn(1)—N(1)	72.99(6)	O(7)—Mn(1)—N(1)	133.80(6)
O(1)—Mn(1)—O(9)	80.27(6)	O(3)—Mn(1)—N(2)	98.64(7)	O(7)—Mn(1)—N(2)	69.89(6)
O(1)—Mn(1)—N(1)	70.78(6)	O(5)—Mn(1)—O(7)	96.55(6)	O(9)—Mn(1)—N(1)	146.10(6)
O(1)—Mn(1)—N(2)	132.95(6)	O(5)—Mn(1)—O(9)	92.30(7)	O(9)—Mn(1)—N(2)	138.49(6)
O(3)—Mn(1)—O(5)	170.44(7)	O(5)—Mn(1)—N(1)	101.06(7)	N(1)—Mn(1)—N(2)	75.41(7)

Table 3

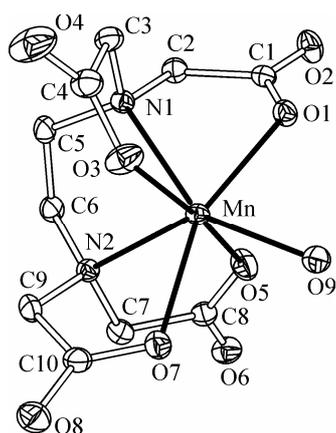
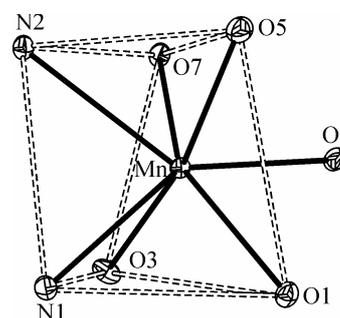
Selected Bond Lengths (Å) and Angles (deg.) in  $(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{cydta})(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$ 

Bond distances (Å)					
Mn—O(2)	2.240(3)	Mn—O(7)	2.264(3)	Mn—N(2)	2.385(4)
Mn—O(4)	2.182(4)	Mn—O(9)	2.272(4)		
Mn—O(6)	2.179(4)	Mn—N(1)	2.350(4)		
Bond angles (deg.)					
O(2)—Mn—O(4)	102.28(14)	O(4)—Mn—O(7)	81.60(14)	O(6)—Mn—N(2)	73.20(15)
O(2)—Mn—O(6)	83.95(15)	O(4)—Mn—O(9)	100.55(15)	O(7)—Mn—O(9)	74.49(13)
O(2)—Mn—O(7)	152.68(13)	O(4)—Mn—N(1)	73.49(14)	O(7)—Mn—N(1)	134.70(13)
O(2)—Mn—O(9)	78.22(13)	O(4)—Mn—N(2)	95.84(15)	O(7)—Mn—N(2)	70.42(13)
O(2)—Mn—N(1)	71.08(13)	O(6)—Mn—O(7)	97.31(16)	O(9)—Mn—N(1)	146.32(14)
O(2)—Mn—N(2)	134.79(14)	O(6)—Mn—O(9)	90.05(16)	O(9)—Mn—N(2)	138.37(14)
O(4)—Mn—O(6)	168.57(15)	O(6)—Mn—N(1)	99.98(16)	N(1)—Mn—N(2)	75.13(14)

Table 4

Selected Bond Lengths (Å) and angles (deg.) in  $\text{K}_2[\text{Mn}^{\text{II}}(\text{Hdtpa})] \cdot 3.5\text{H}_2\text{O}$ 

Bond distances (Å)					
Mn—O(1)	2.1443(18)	Mn—O(9)	2.1238(19)	Mn—N(3)	2.404(2)
Mn—O(5)	2.385(2)	Mn—N(1)	2.414(2)		
Mn—O(7)	2.276(2)	Mn—N(2)	2.360(2)		
Bond angles (deg.)					
O(1)—Mn—O(5)	79.70(7)	O(5)—Mn—O(9)	77.80(8)	O(7)—Mn—N(3)	69.52(7)
O(1)—Mn—O(7)	82.34(7)	O(5)—Mn—N(1)	92.93(7)	O(9)—Mn—N(1)	170.29(7)
O(1)—Mn—O(9)	101.32(8)	O(5)—Mn—N(2)	68.81(7)	O(9)—Mn—N(2)	102.64(8)
O(1)—Mn—N(1)	73.85(7)	O(5)—Mn—N(3)	126.35(7)	O(9)—Mn—N(3)	74.05(8)
O(1)—Mn—N(2)	134.81(7)	O(7)—Mn—O(9)	99.08(8)	N(1)—Mn—N(2)	76.23(7)
O(1)—Mn—N(3)	149.99(8)	O(7)—Mn—N(1)	88.72(7)	N(1)—Mn—N(3)	114.41(7)
O(5)—Mn—O(7)	160.73(7)	O(7)—Mn—N(2)	130.00(7)	N(2)—Mn—N(3)	74.10(8)

Fig. 1. Molecular structure of complex anion in  $(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{edta})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ Fig. 2. Coordination polyhedron around  $\text{Mn}^{2+}$  ion in  $(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{edta})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ 

each edta coordinates to a single  $\text{Mn}^{2+}$  ion with its six donor atoms. As a result, five five-membered rings form. The atoms of each five-membered ring are almost coplanar. The compound  $(\text{NH}_4)_2 \times [\text{Mn}^{\text{II}}(\text{edta})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$  crystallizes in the triclinic system, sp. gr.  $P-1$ , with two formula units in the

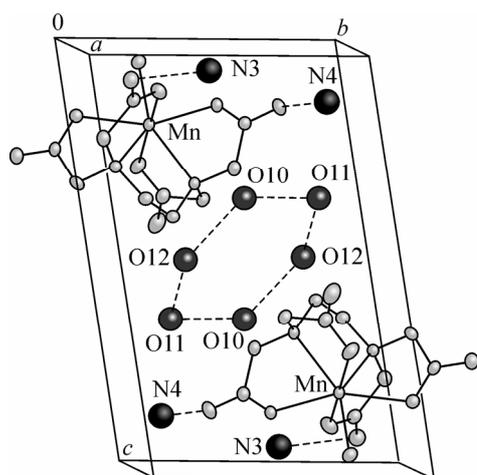


Fig. 3. Unit cell contents of  $(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{edta})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$  (dashed lines represent intermolecular hydrogen bonds)

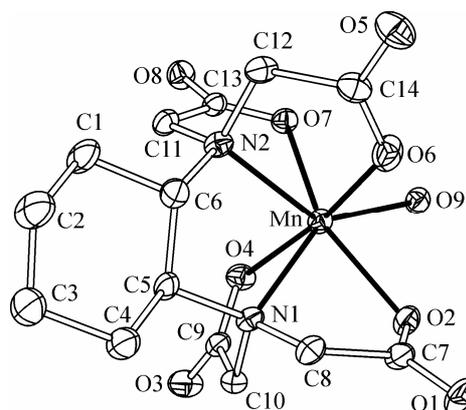


Fig. 4. Molecular structure of complex anion in  $(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{cydta})(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$

unit cell (Fig. 3). The  $[\text{Mn}^{\text{II}}(\text{edta})(\text{H}_2\text{O})]^{2-}$  complex anions are connected by hydrogen bonds to form a layer. The ammonium atom N3 connects to four oxygen atoms through hydrogen bonds, including coordinated O1 and O5 and non-coordinated O6 and O8 which come from three edta ligands, while the ammonium atom N4 connects to three oxygen atoms through hydrogen bonds, including coordinated O3 and non-coordinated O2 and O6 which also come from three edta ligands. Six water molecules link by hydrogen bonds to form a six-membered ring. Such rings are further connected to the complex species.

**$(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{cydta})(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$ .** As shown in Fig. 4, the  $\text{Mn}^{2+}$  ion in the compound is also seven-coordinated, by one cydta ligand and a water molecule. The seven donor atoms, including four carboxyl oxygen atoms and two amine nitrogen atoms, which come from the same cydta ligand, and an oxygen atom from the water molecule, yield a pseudo-monocapped trigonal prismatic configuration. As shown in Fig. 5, the set of N1, O2 and O4 atoms and the set of N2, O6 and O7 atoms form two approximately parallel triangle faces that make the trigonal prism. The seventh donor atom O9 from the water molecule acts as a cap and lies above the face formed by O2, O4, O7 and O6. The average Mn—O bond distance is 2.227(3) Å, which is slightly shorter than the corresponding one in  $[\text{Mn}^{\text{II}}(\text{edta})(\text{H}_2\text{O})]^{2-}$ , the longest bond being 2.272(4) Å (Mn—O9), and the shortest one being 2.179(4) Å (Mn—O6). The Mn—N bond distances are longer than Mn—O. The Mn—N1 and Mn—N2 bond distances are 2.350(4) Å and 2.385(4) Å, respectively. As a hexadentate ligand, each cydta ligand coordinates to a single  $\text{Mn}^{2+}$  ion with its six donor atoms. As a result, five five-membered rings form, similar to the above complex with edta ligand.

The compound  $(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{cydta})(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$  crystallizes in the triclinic system, sp. gr.  $P-1$ , with two formula units in the unit cell (Fig. 6). The  $[\text{Mn}^{\text{II}}(\text{cydta})(\text{H}_2\text{O})]^{2-}$  complex anions are connected through hydrogen bonds involving O9 from the coordinated water molecule, and non-coordinated O1 and coordinated O7 from cydta ligand. The atom N4 of ammonium cation acts as a bridge connecting three oxygen atoms (O2, O6 and O2<sup>#</sup>) by hydrogen bonds, including O2<sup>#</sup> and O6 from one  $[\text{Mn}^{\text{II}}(\text{cydta})(\text{H}_2\text{O})]^{2-}$  complex anion, and O2 from another  $[\text{Mn}^{\text{II}}(\text{cydta})(\text{H}_2\text{O})]^{2-}$  complex anion.

**$\text{K}_2[\text{Mn}^{\text{II}}(\text{Hdtpa})] \cdot 3.5\text{H}_2\text{O}$ .** As shown in Fig. 7, the central  $\text{Mn}^{2+}$  ion in the compound is also seven-coordinated, by seven donor atoms of dtpa ligand, yielding a pseudo-monocapped trigonal prismatic configuration. The donor atoms comprise four carboxyl oxygen atoms and three amine nitrogen atoms, all from the same dtpa ligand. As shown in Fig. 8, the set of N1, N2 and O5 and the set of O7, N3 and O9 form two approximately parallel triangle faces that make a trigonal prism. The seventh donor atom O1 acts as a cap and lies above the face formed by N1, O5, O9 and O7. The average

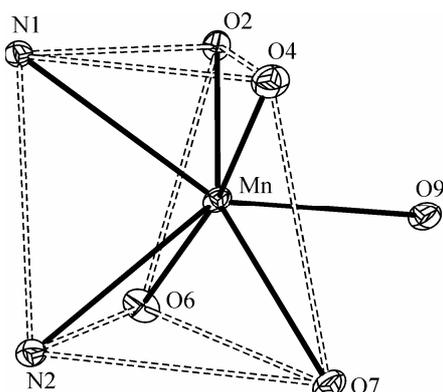


Fig. 5. Coordination polyhedron around  $\text{Mn}^{2+}$  ion in  $(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{cytda})(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$

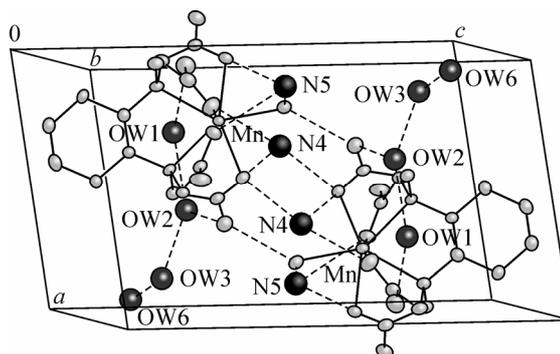


Fig. 6. Unit cell contents of  $(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{cytda})(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$  (dashed lines represent intermolecular hydrogen bonds)

Mn—O bond distance is  $2.232(3) \text{ \AA}$ , which is between the corresponding distances in  $(\text{NH}_4)_2 \times [\text{Mn}^{\text{II}}(\text{edta})(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$  and  $(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{cytda})(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$ , the longest one being  $2.385(2) \text{ \AA}$  (Mn—O5), and the shortest one being  $2.1238(19) \text{ \AA}$  (Mn—O9). The average Mn—N bond distance of  $2.393(2) \text{ \AA}$  is longer than that of Mn—O, with the longest one being  $2.414(2) \text{ \AA}$  (Mn—N1), and the shortest one being  $2.360(2) \text{ \AA}$  (Mn—N2). As a potentially octadentate ligand, each dtpa ligand coordinates to a single  $\text{Mn}^{2+}$  ion using its seven donor atoms. As a result, six five-membered rings form stabilizing the molecular structure. The seven-coordinate Mn—Hdtpa complex contains a non-coordinated, free carboxyl group ( $-\text{COOH}$ ). The  $-\text{COOH}$  group can be modified chemically; for example, it can be used to link the complex to some biological molecules with a specific function such as that of a drug.

The compound  $\text{K}_2[\text{Mn}^{\text{II}}(\text{Hdtpa})]\cdot 3.5\text{H}_2\text{O}$  crystallizes in the triclinic system, sp. gr.  $P-1$ , with two formula units in the unit cell (Fig. 9). Two  $[\text{Mn}^{\text{II}}(\text{Hdtpa})]^{2-}$  complex anions are connected through two potassium cations ( $\text{K1}$  and  $\text{K1}^{\#}$ ) and hydrogen bonds through six water oxygen atoms ( $\text{OW12}$ ,  $\text{OW12}^{\#}$ ,  $\text{OW13}$ ,  $\text{OW13}^{\#1}$ ,  $\text{OW13}^{\#2}$ ,  $\text{OW13}^{\#3}$ ). The atom  $\text{K1}$  is coordinated by nine oxygen atoms and acts as a bridge connecting O1 and O10 atoms from two dtpa ligands. The atom  $\text{K2}$  is coordinated by eight oxygen atoms of which three atoms ( $\text{OW11}$ ,  $\text{OW13}$  and  $\text{OW13}^{\#}$ ) come from crystallization water molecules and others come from two adjacent dtpa ligands. These two potassium cations and two more potassium cations generated by the center of symmetry take part in connecting the two adjacent anions. The distances between  $\text{K1}$  and  $\text{K2}$  is  $5.783 \text{ \AA}$  and between  $\text{K1}^{\#}$  and  $\text{K2}$  (or between  $\text{K1}$  and  $\text{K2}^{\#}$ ) is  $4.162 \text{ \AA}$ . The atom  $\text{OW14}$  of a water molecule connects two  $[\text{Mn}^{\text{II}}(\text{Hdtpa})]^{2-}$  complex anions of

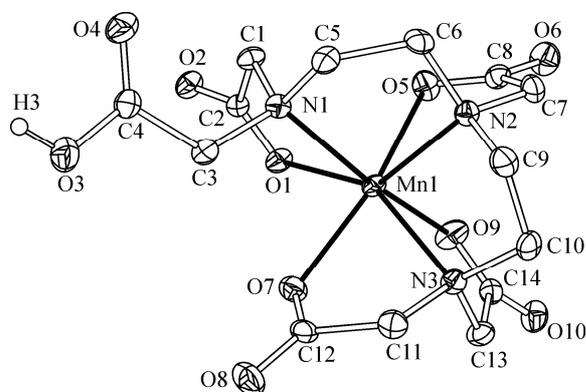


Fig. 7. Molecular structure of complex anion in  $\text{K}_2[\text{Mn}^{\text{II}}(\text{Hdtpa})]\cdot 3.5\text{H}_2\text{O}$

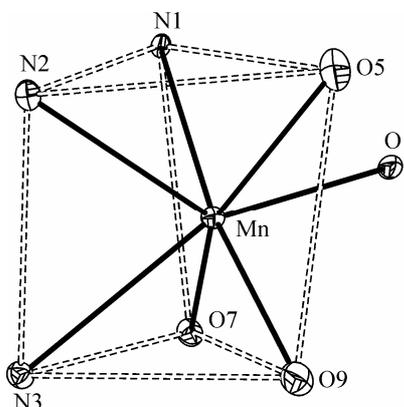


Fig. 8. Coordination polyhedron around  $\text{Mn}^{2+}$  ion in  $\text{K}_2[\text{Mn}^{\text{II}}(\text{Hdtpa})]\cdot 3.5\text{H}_2\text{O}$

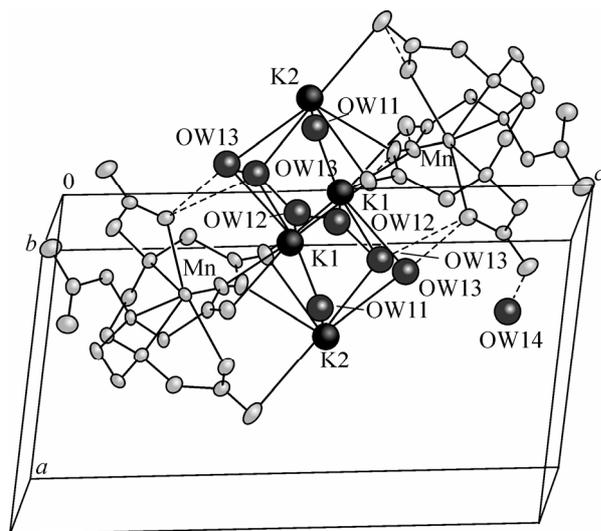


Fig. 9. Unit cell contents of  $\text{K}_2[\text{Mn}^{\text{II}}(\text{Hdtpa})] \cdot 3.5\text{H}_2\text{O}$  (dashed lines represent intermolecular hydrogen bonds)

the same layer through hydrogen bonds additionally stabilizing the structure.

### CONCLUSIONS

New complexes of  $\text{Mn}^{2+}$  with edta, cydta and dtpa ligands were prepared; their compositions and structures were determined by elemental analysis and single-crystal X-ray diffraction technique. As a result of this study, the compounds were formulated as  $(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{edta})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{cydta})(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$  and  $\text{K}_2[\text{Mn}^{\text{II}}(\text{Hdtpa})] \cdot 3.5\text{H}_2\text{O}$ . All the three complexes

adopt seven-coordinate pseudo-monocapped trigonal prismatic configuration. In the  $\text{K}_2[\text{Mn}^{\text{II}}(\text{Hdtpa})]$  complex, there is a free, non-coordinated carboxyl group. In contrast, the complexes with edta and cydta have the  $\text{Mn}^{2+}$  ion coordinated with an edta or cydta ligand and an additional, water molecule. The crystal structures of the three complexes are all of layered type and the compounds isolated are water-soluble.

### SUPPLEMENTARY MATERIAL

CCDC 635765 —  $(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{edta})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ , CCDC 635766 —  $(\text{NH}_4)_2[\text{Mn}^{\text{II}}(\text{cydta})(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$  and CCDC 635767 —  $\text{K}_2[\text{Mn}^{\text{II}}(\text{Hdtpa})] \cdot 3.5\text{H}_2\text{O}$  contain the supplementary crystallographic data for this article. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), by e-mailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033.

### ACKNOWLEDGEMENT

The authors greatly acknowledge The National Natural Science Foundation of China (N 20371023) and The Natural Science Foundation of Educational Department of Liaoning Province (N 2004C018) for financial support. The authors also thank their colleagues and students participating in this work.

### REFERENCES

1. Li Z.F., Li W.S., Li X.J. *et al.* // *J. Inorg. Biochem.* – 2007. – **101**, N 7. – P. 1036.
2. Thunus L., Lejeune R. // *Coord. Chem. Rev.* – 1999. – **184**, N 1. – P. 125.
3. Meade T.J., Taylory A.K., Bullz S.R. // *Curr. Opin. Neurobiol.* – 2003. – **13**, N 3. – P. 597.
4. Aime S., Anelli P., Botta M. *et al.* // *J. Biol. Inorg. Chem.* – 2002. – **7**, N 1-2. – P. 58.
5. Wang J., Zhang X.D., Wang Y. *et al.* // *Chin. J. Struct. Chem.* – 2004. – **23**, N 8. – P. 890.
6. Wang J., Wang Y., Zhang X.D. *et al.* // *Ibid.* – N 10. – P. 1169.
7. Wang J., Wang Y., Zhang X.D. *et al.* // *Ibid.* – N 12. – P. 1420.
8. Wang J., Zhang X.D., Zhang Y. *et al.* // *J. Struct. Chem.* – 2004. – **45**, N 1. – P. 114.
9. Wang J., Zhang X.D., Wang Y. *et al.* // *Ibid.* – N 6. – P. 1022.
10. Wang J., Gao G.R., Zhang Z.D. *et al.* // *Russ. J. Coord. Chem.* – 2007. – **33**, N 4. – P. 258.
11. Wang J., Zhang X.D., Ling X. *et al.* // *J. Mol. Struct.* – 2002. – **611**, N 2. – P. 39.
12. Wang J., Zhang X.D., Jia W.G. // *Acta. Chim. Sinica.* – 2002. – **60**, N 8. – P. 1452.
13. Mizuta T., Wang J., Miyoshi K. // *Bull. Chem. Soc. Jpn.* – 1993. – **66**. – P. 2547.
14. Mizuta T., Wang J., Miyoshi K. // *Inorg. Chim. Acta.* – 1993. – **203**. – P. 249.
15. Wang J., Liu X.Zh., Wang X.F. *et al.* // *J. Struct. Chem.* – 2007. – **48**.
16. Krenning E.P., Bakker W.H., Kooij P.P.M. *et al.* // *J. Nucl. Med.* – 1992. – **33**, N 5. – P. 652.
17. Sheldrick G.M., SHELXTL Programs, version 5.1, Bruker AXS GmbH, Karlsruhe, Germany, 1998.