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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF TRIS[4-(2-PYRIDYLMETHYLENEAMINO)-PHENOL]MANGANESE(II)BIS(PERCHLORATE)

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În compusul [Mn($C_{12}H_{10}N_2O$)$_3$](ClO_4)$_2$, ionul metalic adoptă o geometrie octaedrică deformată, fiind coordinat cu şase atomi de azot de la cei trei liganzi bidentaţi din sfera de coordinare, formând izomerul meridional (OC-6-21). În complexul mononuclear al Mn(II) apar două legături de hidrogen intermoleculare O-H···O între grupările hidroxil ale liganzilor şi anionii perclorat.

Compusul descris aici este izomorf cu [Fe($C_{12}H_{10}N_2O$)$_3$](ClO_4)$_2$, un compus descris de noi anterior [12].

In the title compound, [Mn($C_{12}H_{10}N_2O$)$_3$](ClO_4)$_2$, the metal center is coordinated by six N atoms from the three bidentate chelating ligands in a distorted octahedral coordination geometry, with overall formation of the meridional (OC-6-21) isomer. In the mononuclear Mn(II)-complex there are two intermolecular O-H···O hydrogen bonds between the hydroxyl groups of the cation and the counter-anions.

The title compound is isomorphous with [Fe($C_{12}H_{10}N_2O$)$_3$](ClO_4)$_2$, a compound reported by us previously [12].

Keywords: Schiff bases, manganese complexes, single-crystal X-ray study, isomorphism

1. Introduction

A large number of Schiff bases and their complexes have been studied for their interesting and important properties, e.g., the ability to reversibly bind oxygen,

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catalytic activity in the hydrogenation of olefins, photochromic properties, complexing ability towards transition metals and so on [1]. Synthesis of new Schiff bases and their metal complexes still is the aim of many recent investigations [2-4].

We report here the preparation of Mn(II) complex with a Schiff base ligand, 2-pyridinecarboxaldehyde(*p*-hydroxyphenylimine), and its structural characterization.

Like 2,2'-bipyridine and 1,10-phenanthroline, Schiff bases derived from 2-pyridine-carboxaldehyde provide the π-acidic α,α'-diimine fragment for metal coordination.

2. Experimental

Attempts to synthesise manganese(II) complexes with the Schiff base ligand, 2-pyridinecarboxaldehyde(*p*-hydroxyphenylimine) for a molar ratio M:L 1:2 or 1:3 gave the same crystalline complex $[Mn(C_{12}H_{10}N_2O)_3](ClO_4)_2$, in which Mn^{II} has a distorted octahedral coordination geometry comprising six N atoms from the three bidentate chelating ligands.

The ligand (2-pyridinecarboxaldehyde(*p*-hydroxyphenylimine)) was prepared following the procedure developed in literature [5].

Stoichiometric amounts of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.362 g, 1 mmol) and (2-pyridinecarboxaldehyde(*p*-hydroxyphenylimine)) (0.594 g, 3 mmol) were dissolved in acetonitrile (40 ml) and stirred under reflux to promote the complete formation of the complex $[Mn(C_{12}H_{10}N_2O)_3](ClO_4)_2$, **1**.

Single crystals suitable for X-ray diffraction studies have been obtained by slow diffusion at room temperature in diisopropyl ether.

Anal. Calcd. for $C_{36}H_{30}Cl_2MnN_6O_{11}$: H: 3.56, C: 50.96, N: 9.90; Found: H: 3.97, C: 50.04, N: 9.76.

3. Results and discussion

The title complex has been prepared and structurally characterized. The central Mn atom is coordinated by three ligand molecules through the nitrogen atoms in a bidentate manner (Figure 1). The coordination geometry is distorted octahedral. The complex crystallizes as the meridional isomer in the monoclinic centrosymmetric space group $P2_1/c$. The meridional isomer is associated with two different orientations of the bidentate ligands in a 2:1 distribution (Figure2). These two types of geometry are reflected in different dihedral angles between the aromatic and heteroaromatic rings. The dihedral angles are 44.4(6)° (in N1···N2 bidentate ligand), 28.7(6)° (in N3···N4 bidentate ligand) and 18.8(5)° (in N4···N5 bidentate ligand). The distances Mn(II)-N (pyridine) are shorter than the Mn(II)-N (imine), **Table 1**.

Table 1

Selected distances and angles for **1**

	Distances, Å		
Mn(1)-N(1)	2.207(10)	Mn(1)-N(2)	2.340(10)
Mn(1)-N(3)	2.236(9)	Mn(1)-N(4)	2.292(9)
Mn(1)-N(5)	2.254(10)	Mn(1)-N(6)	2.255(9)
	Angles, °		
N(1)-Mn(1)-N(3)	164.4(3)	N(5)-Mn(1)-N(4)	94.7(4)
N(1)-Mn(1)-N(5)	101.1(4)	N(6)-Mn(1)-N(4)	165.5(3)
N(3)-Mn(1)-N(5)	91.7(3)	N(1)-Mn(1)-N(2)	73.1(4)
N(1)-Mn(1)-N(6)	96.6(3)	N(3)-Mn(1)-N(2)	93.0(4)
N(3)-Mn(1)-N(6)	95.2(3)	N(5)-Mn(1)-N(2)	170.8(4)
N(5)-Mn(1)-N(6)	75.5(4)	N(6)-Mn(1)-N(2)	111.9(4)
N(1)-Mn(1)-N(4)	95.9(3)	N(4)-Mn(1)-N(2)	79.0(3)
N(3)-Mn(1)-N(4)	74.1(3)		

Electroneutrality of the complex is achieved by uncoordinated perchlorate anions. ClO_4^- was classified as a non-coordinating anion and its very weak basicity is correlated to the very strong acidity of $HClO_4$ (pK =−18) [6]. A CSD [7] database search shows that out of 14899 compounds containing perchlorate anion, in 13600 compounds the perchlorate is uncoordinated (error free entries in the database without disorder, total number of entries in the database is 436384). The perchlorate anion has C1--O distances in the range of 1.419(13)-1.452(10) Å and O--C1--O angles in the range of 104.7(7)-114.7(8)°.

In the mononuclear Mn(II)-complex there are two intermolecular O-H···O hydrogen bonds between the hydroxyl groups of the cation and the counter-anions (d(O···O) = 2.791(12) Å and 2.771(12) Å, **Table 2**).

Table 2

Hydrogen-bond geometry (Å ,°)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O(1) --H(1)···O(8)^{i}	0.98	2.13	2.791(12)	124
O(2) --H(2)···O(5)^{ii}	0.98	1.90	2.771(12)	146

^{i}= -x,1/2+y,1/2-z; ^{ii} = x,1/2-y,1/2+z;

X-ray structure determination

For intensity data collection a single crystal of **1** was mounted on a glass fiber and placed directly in a cold stream of dinitrogen. Crystal data, parameters in data collection and convergence results are listed in **Table 3**.

Table 3

Experimental X-ray diffraction parameters and crystal data for 1

	1
Empirical formula	$C_{36}H_{30}Cl_2MnN_6O_{11}$
Moiety formula	$C_{36}H_{30}MnN_6O_3$, 2(ClO_4)
Formula mass	848.50
Crystal habit, color	rod, dark brown
Crystal dim. (mm)	0.18 x 0.05 x 0.04
Crystal system	Monoclinic
Space Group	$P2_1/c$
a [Å]	16.314(4)
b [Å]	8.880(2)
c [Å]	24.983(7)
ß [°]	90.519(8)
V [Å^3]	3619.1(16)
Z	4
D [g.cm^{-1}]	1.557
F000	1740
μ(Mo-K_α) [mm^{-1}]	0.584
Diffractometer	Bruker Smart CCD
T [K]	130(2)
θ range	2.43– 25.00
Refl. collected	6910
Unique refl.	4429
R_{int}	0.1257
Reflections I>2σ(I)	1716
Parameters refined	243
R_1	0.0973
wR_2	0.2312
GooF	1.018
Diff. peak/ hole [e/Å^3]	0.795/ - 0.548

Data collection was performed at 130 K with a Bruker Smart APEX CCD (Mo-K_α radiation, λ= 0.71073 Å, graphite monochromator) area detector. The unit cell parameters were obtained by least-squares refinement of 291 reflections. The structure was solved by direct methods (SHELXS-97) [8] and refined by full matrix least-squares procedures based on F^2 with all measured reflections (SHELXL-97) [9]. The SADABS [10] program was used for absorption correction. Mn and Cl atoms were refined anisotropically, other non-hydrogen atoms isotropically and H atoms were introduced in their idealized positions (*d*C–H = 0.98 Å) and were refined using a riding model.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 699839. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: int. code + (1223) 336-033; e-mail: deposit@ccdc.cam.ac.uk; web, www: http://www.ccdc.cam.ac.uk).

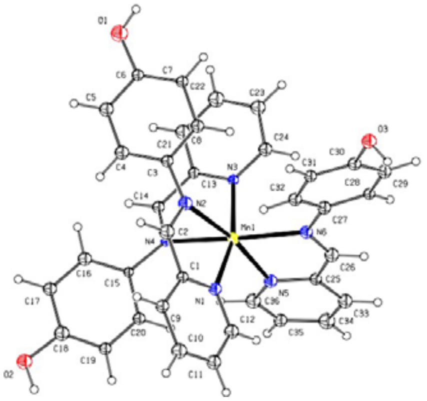

Fig. 1. The molecular structure of the title dication, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability [11] level and H atoms are represented by spheres of arbitrary radius.

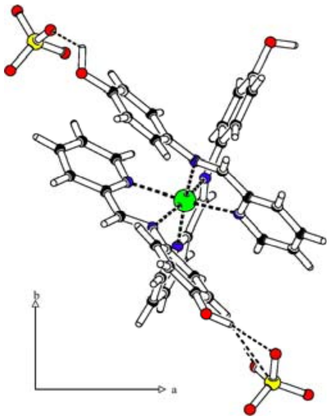

Fig. 2. View of the asymmetric unit along the *c* axis. H-bonds included.

The title compound is isomorphous with $[Fe(C_{12}H_{10}N_2O)_3](ClO_4)_2$, a compound previously reported by us [12]. Although $[Mn(C_{12}H_{10}N_2O)_3](ClO_4)_2$ and $[Fe(C_{12}H_{10}N_2O)_3](ClO_4)_2$ are isomorphous, the first one is a mononuclear complex, while in the iron (II) complex, the intermolecular O—H···O hydrogen bonds between the OH groups of the cation and the anions form an infinite onedimensional chain in the *c* direction. In first case, the perchlorate acts as a counteranion, while in the second complex, one perchlorate anion acts as a counteranion and the second one acts as a bridge between two cations (*Figure 3*).

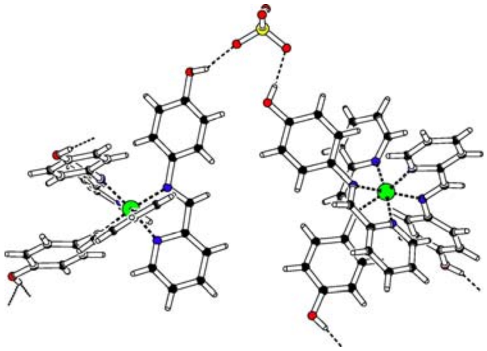

Fig. 3. Crystal structure of $[Fe(C_{12}H_{10}N_2O)_3](ClO_4)_2$.

4. Conclusions

A new Mn(II)-Schiff base complex, **1** was synthesised and structurally characterized. The complex is isomorphous with $[Fe(C_{12}H_{10}N_2O)_3](ClO_4)_2$. This is a good example of isomorphism in compounds, which have different structures with respect of intermolecular interactions.

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