



# PHYSICAL CHEMISTRY 2004

## *Proceedings*

*of the 7<sup>th</sup> International Conference  
on Fundamental and Applied Aspects of  
Physical Chemistry*

*Volume I and II*

September 21-23, 2004  
Belgrade, Serbia and Montenegro



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Editors

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ISBN 86-82457-12-x  
Title: Physical Chemistry 2004. (Proceedings)  
Editors A. Antić-Jovanović and S. Anić  
Published by: The Society of Physical Chemists of Serbia, Student-  
ski trg 12-16, P.O.Box 137, 11001 Belgrade, Serbia  
and Montenegro  
Publisher: Society of Physical Chemists of Serbia  
Printed by: "Jovan" Printing and Published Comp;  
300 Copies; Number of Pages: x + 906; Format B5;  
Printing finished in September 2004.  
Text and Layout: Aleksandar Nikolić

*300 – copy printing*

# CRYSTAL AND ABSOLUTE STRUCTURE OF THE AQUADICHLORO(PYRIDOXAL THIOSEMICARBAZONE) IRON(III) CHLORIDE

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## Abstract

A new Fe(III) complex of pyridoxal thiosemicarbazone (H<sub>2</sub>L) has been characterized by single-crystal X-ray analysis. The Fe atom in the title complex, [Fe(H<sub>2</sub>L)Cl<sub>2</sub>(H<sub>2</sub>O)]Cl, has a distorted octahedral configuration formed by NSO<sub>2</sub>Cl<sub>2</sub> donor set. Six-membered chelate ring significantly deviates from planar form. The crystal structure is stabilized by weak intermolecular C-H... $\pi$  interaction directed towards the center of the pyridine ring.

## Introduction

Transition metal complexes of thiosemicarbazones of different denticity are great interest because of their chemical, structural and pharmacological properties [1,2]. Tridentate (ONS) pyridoxal thiosemicarbazone H<sub>2</sub>L ( Fig.1 ) is an interesting ligand which can be easily prepared by reacting of pyridoxal, e.g. 3-hydroxy-2-hydroxymethyl-2-methylpyridine-4-carbaldehyde (one of the forms of vitamine B<sub>6</sub>) with thiosemicarbazide [3]. With this ligand a substantial number of metal complexes has been synthesized [4], among them some Fe(III) complexes. Namely, the synthesis, spectroscopic and voltammetric characteristics of Fe(III) complexes, including other with pyridoxal Schiff bases derivatives, of the formulas Fe(H<sub>2</sub>L)Cl<sub>3</sub>·H<sub>2</sub>O and [Fe(HL)<sub>2</sub>]Cl were described in [5]. Besides, the crystal structure of the square pyramidal [Fe(HL)Cl<sub>2</sub>] complexes was referred in [6]. This work reports the crystal and molecular structures of octahedral [Fe(H<sub>2</sub>L)Cl<sub>2</sub>(H<sub>2</sub>O)]Cl complex determined by X-ray structural analysis.

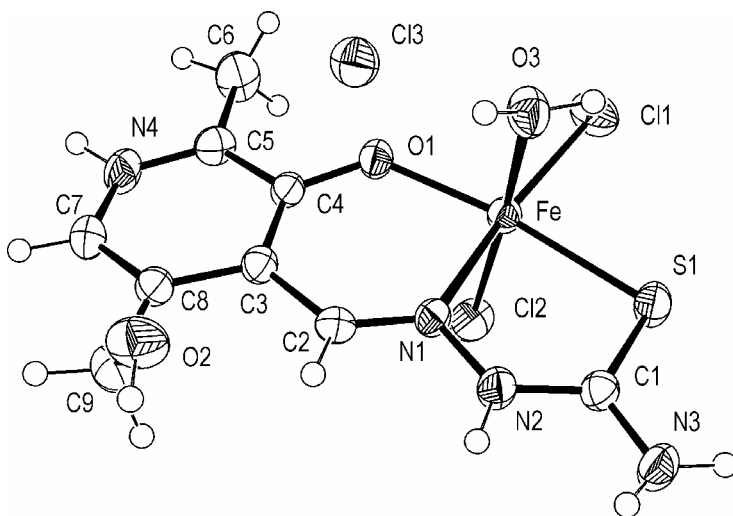
## Experimental

Black monocrystals of the title complex were obtained by the reaction of a warm dilute EtOH solution of the protonated form of the ligand H<sub>2</sub>L·HCl·H<sub>2</sub>O (5), and FeCl<sub>3</sub>·6H<sub>2</sub>O in a 1:1,2 molar ratio, respectively.

The X-ray data were collected on an Enraf-Nonius CAD-4 diffractometer by using graphite-monochromated MoK $\alpha$  (0.71073 Å) radiation at 293(2) K. Cell constants and orientation matrix were obtained from 24 centered reflections (13.17° to 16.70°  $\theta$  range) corresponded to a orthorhombic cell whose parameters are: a = 7.304(2) Å, b = 8.401(2) Å, c = 25.359(7) Å,  $\alpha = \beta = \gamma = 90^\circ$ , V = 1556.2(7) Å<sup>3</sup>. A total of 2743 reflections (1.61° to 25.97°  $\theta$  range) were collected by using  $\omega/2\theta$  scans. The data were corrected for Lorentz and polarization effects. A gaussian-type absorp-

tion correction based on the crystal morphology was successfully applied ( $T_{\min} = 0.5930$ ,  $T_{\max} = 0.8507$ ). The positions of Fe and Cl atoms were solved by the heavy-atom method in the  $P2_12_12_1$  space group. The rest of non-hydrogen atoms was determined by difference Fourier methods and refined anisotropically (together with Fe and Cl atoms) on the  $F^2$  by full-matrix least-square method to  $R1 = 0.0281$  and  $Rw = 0.0805$  for 218 refined parameters and 2258 reflections with  $I > 2\sigma(I)$ . The final difference map was with the largest residual peak and hole of 0.348 and  $-0.300 \text{ e.}\text{\AA}^{-3}$  respectively.

All of seven H atoms bonded to N and O were determined by difference Fourier method. Their positions and isotropic temperature parameters were freely refined. The rest of H atoms, bonded to carbon atoms, were placed geometrically and refined with a riding model, and with  $U_{\text{iso}}$  constrained to  $U_{\text{eq}}$  of the carrier atom. Crystallographic data: formula  $\text{C}_9\text{H}_{14}\text{Cl}_3\text{SN}_4\text{O}_3\text{Fe}$ , orthorhombic, space group  $P2_12_12_1$ ,  $Z = 4$ ,  $D_c = 1.795 \text{ g/cm}^3$ ,  $\mu = 1.631 \text{ mm}^{-1}$ , crystal size = 0.42 x 0.36 x 0.10 mm.



**Fig. 1.** Perspective view of the crystal structure of  $[\text{Fe}(\text{H}_2\text{L})\text{Cl}_2(\text{H}_2\text{O})]\text{Cl}$  complex showing 50% probability displacement ellipsoids and the atom-numbering scheme.

## Result and Discussion

Absolute structure of  $[\text{Fe}(\text{H}_2\text{L})\text{Cl}_2(\text{H}_2\text{O})]\text{Cl}$  complex has been correctly assigned what was confirmed by the Flack absolute structure parameter  $x = -0.01(3)$ . The Fe(III) is sited in an octahedral environment. The equatorial plane is formed by a tridentate coordination of the  $\text{H}_2\text{L}$  ligand and one Cl atom, while the next Cl atom and one water molecule are in axial positions (Fig. 1). The Fe-Cl2 bond distance [2.2990(13) Å] is longer than it is for the Fe-Cl1 bond [2.2740(13) Å]. Coordination geometry is significantly deformed, for instance, the Fe atom is displaced by 0.167(1) Å from the N1/S1/Cl1/O1 coordination plane toward the apical Cl2 atom. The Cl1-Fe-Cl2 coordination angle is  $97.73(5)^\circ$  what is much higher than  $90^\circ$ .

The six-membered chelate ring adopts non-planar form with total puckering amplitude of 0.202(3) Å. It is a surprise regarding that tridentate thiosemicarbazide-based ligands usually form planar chelate rings. In the present case of [Fe(H<sub>2</sub>L)Cl<sub>2</sub>(H<sub>2</sub>O)]Cl complex six-membered chelate ring is mainly distorted around Fe-O1 bond (The N1-Fe-O1-C4 torsion angle is 23°). This structural behavior has important consequences in the conformation of complex cation presented by existing absolute structure. Thus the interplanar angle between mean plane of N1S1Cl1O1 and mean plane of pyridine ring is 11.1(2)°. In that way the C5 atom is displaced by 0.552(7) Å from equatorial coordination plane.

The crystal packing consists of 2D-layers parallel to (001) crystallographic plane. Within the layers neighboring molecules form weak intermolecular interactions and hydrogen bonds. The Cl3 anions are located between 2D-layers interconnected them by hydrogen bonds which are the strongest among those indicated in the present crystal structure. The C6-methyl group form weak intermolecular C-H... $\pi$  interaction directed towards the center of the pyridine ring. The same type of C-H... $\pi$  interaction was observed in the crystal structure of Cu(II) with pyridoxal isothiosemicarbazone [7].

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