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Transition metal complexes with thiosemicarbazide-based ligands. Part 45. Synthesis, crystal and molecular structure of [2,6-diacetylpyridine bis(S-methylisothiosemicarbazonato)]diazide-iron(III)*

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Abstract: The template reaction of a warm methanolic solution of $FeCl_3 \cdot 6H_2O$, S-methylisothiosemicarbazidehydroiodide and 2,6-diacetylpyridine in the presence of LiOAc and NaN_3 yielded the high-spin complex $[Fe(HL)(N_3)_2]$, were HL is the monoanion of the ligand 2,6-diacetylpyridine bis(S-methylisothiosemicarbazone). X-Ray analysis of the complex showed its pentagonal-bipyramidal configuration, with pentadenate (N_5) HL in the equatorial plane and two monodentate azide groups in the axial positions. Crystal data are: monoclinic, $P2_1/c$, $a = 1.0263(2)$, $b = 1.2525(2)$, $c = 1.6660(3)$ nm, $\beta = 98.94^\circ$, $V = 2.1154$ nm^3, $Z = 4$, $\rho_x = 1.499$ g cm^{-3}, $\rho_0 = 1.48$ g cm^{-3}, F(000) = 984, $\mu = 9.40$ cm^{-1}.

Keywords: iron(III) complex, 2,6-diacetylpyridine bis(S-methylisothiosemicarbazone) azide, crystal structure.

INTRODUCTION

A very large number of metal complexes involving thiosemicarbazide derivatives as ligand have been prepared and studied,[1–6] including also mixed macrocyclic complexes containing crown ether moieties.[5] From the point of view of denticity, a special place among them occupy the potentially pentadentate 2,6-diacetylpridine bis(thiosemi/isothiosemicarbazones), involving N_3S_2 and N_5 sets of donor atoms, respectively, occupy a special place among them.[3,4,6] These type of ligands are interesting because of their ability to form heptacoordinated pentagonal-bipyramidal (PBP) complexes even with some 3d-elements which charactistically do not form such complexes.[6,7] Namely, these planar, pentadentate ligands occupy the equatorial plane while the PBP surroundings of the metal is completed with two monodentate ligands at the axial positions.

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[*] Dedicated to Professor Miroslav J. Gašić on the ocassion of his 70th birthday.

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In our previous work,[8] the syntheses and some physico-chemical characteristics of Co(II), Mn(II) and Zn(II) complexes with 2,6-diacetylpyridine bis(S-methylisothiosemicarbazone) (H_2L, Fig. 1) of the general formula $M(H_2L)I_2 \cdot nS$ ($S = H_2O$, MeOH), as well as Ni(HL)I were described. A PBP configuration was ascribed to the complexes of Co(II), Mn(II) and Zn(II) while a penta coordinated structure was assumed for the Ni(II) complex.

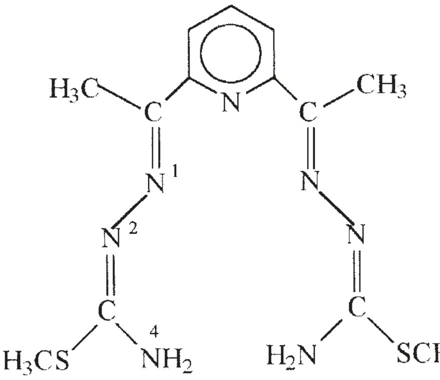

Fig. 1. Structural formula of 2,6-diacetylpyridine bis(S-methylisothiosemicarbazone).

The solved crystal structures of $[Mn(H_2L)NCS(MeOH)]NCS$ that was later synthesized[9] and of the mentioned nickel complex[10] confirmed all the above assumptions. Namely, it was found that manganese complex has a PBP configuration involving the neutral pentadentate N_5 ligand H_2L in the equatorial plane and a NCS group and MeOH at the axial positions. In the square-pyramidal nickel complex, the ligand monoanion is coordinated in a way that is unexpected for the isothiosemicarbazide derivatives. Namely, the ligand behaves as a tetradentate (N_4) entity, whereby one of the isothiosemacarbazide moieties is coordinated as monodentate in an unusual way, *i.e.*, *via* the hydrazine nitrogen atom N2.

This work deals with the crystal structure of the newly-syntesized PBP complex of iron(III) of the formula $[Fe(HL)(N_3)_2]$, in which the monoanion 2,6-diacetylpyridine bis(S-methylisothiosemicarbazone) is coordinated in the usual way, *i.e.*, *via* the pyridine nitrogen atom and nitrogen atoms N1 and N4 of both the isothiosemicarbazide fragments.

EXPERIMENTAL

Preparation of the complex

A mixture of 0.27 g (1 mmol) of $FeCl_3 \cdot 6H_2O$, 0.46 g (2 mmol) of S-methylisothiosemicarbazidehydroiodide,[11] 0.16 g (1 mmol) of 2,6-diacetylpyridine and 0.20 g (2 mmol) of $LiOAc \cdot 2H_2O$ was dissolved in 5 cm^3 of MeOH with heating. After 5 h a product of undefined composition was filtered and dissolved with heating in 40 cm^3 of MeOH, and filtered. To the warm filtrate, a warm and filtered solution of 0.20 g of NaN_3 in 20 cm^3 of MeOH was also added. After 15 h, the formed black crystals were filtered and washed with MeOH. Yield: 0.24 g. Anal. Found: C, 33.56; H, 3.68; N, 38.17 %. Calcd for $FeC_{13}H_{18}N_{13}S_2$ ($M_r = 476.33$): C, 32.78; H, 3.81; N, 38.23 %.

Analytical methods

Elemental (C, H, N) analysis was carried out by standard micromethods in the Centre for Instrumental Analysis, Faculty of Chemistry, Belgrade.

*IR spectr*a (KBr disc) were run on a Perkin-Elmer FTIR 31725X instrument.

Magnetic susceptibility measurements were made at room temperature using a magnetic susceptibility balance MSB-MKI (Sherwood Scientific Ltd., Cambridge, England). The data were corrected for diamagnetic susceptibilities.

The molar conductivity of a freshly-prepared 1×10^{-3} mol/dm^3 solution in DMF was measured on a Jenway 4010 conductivity meter.

X-Ray analysis. The black prismatic monocrystals of the title complex were investigated by the X-ray diffraction methods. The space group $P2_1/c$ was determined from the systematic absences of (*hkl*). The X-ray diffraction intensity measurement was done on a monocrystal (0.8×0.3×0.3 mm) at room temperature (T = 291 K) on an Enraf-Nonius CAD-4 diffractometer using MoKα radiation (λ = 0.071069 nm), monocromatized with a graphite monochromator and the ω-2θ scan mode. The cell constants were determined and refined by the least squares treatment of the diffractometer setting angles of 52 strong reflections in the 2θ range of 20–25º. An extinction correction was not necessary. The crystal data are: monoclinic, $P2_1/c$, a = 1.0263(2), b = 1.2525(2), c = 1.6660(3) nm, β = 98.94º, V = 2.1154 nm^3, Z = 4, ρ_x = 1.499 g cm^{-3}, ρ_0 = 1.48 g cm^{-3}, $F(000)$ = 984, μ = 9.40 cm^{-1}.

A total of 3958 reflections were measured in the range $4º \leq 2\theta \leq 50º$ (three check reflections with no significant intensity variation). After the systematic absences had been deleted, the merging of equivalent reflections gave 2634 unique reflections (R_{int} = 0.0248) of whichi 1911 with $F > 3\sigma(F)$ were used for all calculations.[12] The data were corrected for the Lorentz and polarization effects, but not for absorption.

TABLE I. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters U_{eq}*/nm$^2 \times 10^4$

	x	*y*	*z*	U_{eq}
Fe	6305(1)	971(1)	1840(1)	29(1)
S(4')	2214(2)	1429(1)	96(1)	52(1)
S(4")	7989(2)	4148(1)	2899(1)	46(1)
N(1)	7152(5)	–651(3)	2127(2)	28()
N(2')	5044(5)	–317(3)	1146(2)	27(2)
N(2")	8152(5)	1094(3)	2727(2)	33(2)
N(3')	3932(5)	14(3)	643(3)	32(2)
N(3")	8569(6)	2075(3)	3030(3)	36(2)
N(5')	4537(5)	1663(3)	1157(2)	32(2)
N(5")	6715(6)	2537(3)	2103(3)	34(2)
N(11)	7296(6)	961(3)	837(3)	36(2)
N(12)	8202(7)	1544(4)	799(3)	59(3)
N(13)	9056(9)	2117(7)	736(5)	123(4)
N(21)	5318(6)	698(3)	2811(3)	39(2)
N(22)	5376(6)	–60(3)	3234(3)	39(2)
N(23)	5436(7)	–791(4)	3664(3)	68(3)
C(2)	6518(6)	–1524(3)	1793(3)	29(2)
C(3)	7023(7)	–2545(4)	2002(3)	35(2)

TABLE I. Continued

	x	*y*	*z*	U_{eq}
C(4)	8164(7)	–2635(4)	2531(3)	42(3)
C(5)	8815(7)	–1745(4)	2878(3)	39(2)
C(6)	8246(7)	–747(3)	2664(3)	32(2)
C(1’)	5300(7)	–1322(3)	1235(3)	28(2)
C(1”)	8803(7)	265(4)	3028(3)	33(2)
C(11’)	4461(7)	–2196(4)	833(3)	45(3)
C(11”)	9926(8)	305(5)	3686(4)	58(3)
C(4’)	3701(6)	1090(4)	694(3)	29(2)
C(4”)	7716(7)	2785(4)	2645(3)	33(2)
C(41’)	2191(8)	2847(4)	174(3)	59(3)
C(41”)	9339(8)	4109(4)	3729(3)	53(3)

*Equivalent isotropic U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor

TABLE II. Bond lengths/nm×10^4

Fe-N(1)	2232(4)	Fe-N(2’)	2269(4)
Fe-N(2”)	2221(5)	Fe-N(5’)	2167(5)
Fe-N(5”)	2039(4)	Fe-N(11)	2088(5)
Fe-N(21)	2066(5)	S(4’)-C(4’)	1740(6)
S(4’)-C(41’)	1781(6)	S(4”)-C(4”)	1771(5)
S(4”)-C(41”)	1800(6)	N(1)-C(2)	1348(6)
N(1)-C(6)	1329(7)	N(2’)-N(3’)	1371(6)
N(2’)-C(1’)	1290(6)	N(2”)-N(3”)	1371(5)
N(2”)-C(1”)	1293(7)	N(3’)-C(4’)	1374(6)
N(3”)-C(4”)	1339(7)	N(5’)-C(4’)	1280(7)
N(5”)-C(4”)	1296(8)	N(11)-N(12)	1192(8)
N(12)-N(13)	1150(11)	N(21)-N(22)	1179(6)
N(22)-N(23)	1157(6)	C(2)-C(3)	1403(7)
C(2)-C(1’)	1459(8)	C(3)-C(4)	1356(9)
C(4)-C(5)	1380(8)	C(5)-C(6)	1402(7)
C(6)-C(1”)	1480(7)	C(1’)-C(11’)	1486(7)
C(1”)-C(11”)	1463(9)		

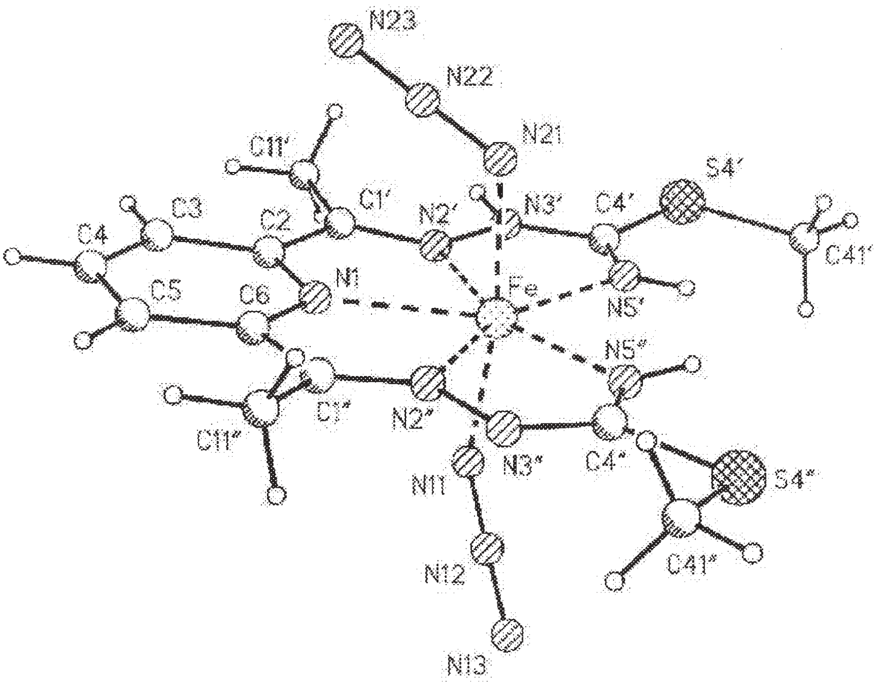

Fig. 2. Perspective view of the [Fe(HL)$(N_3)_2$] complex with labeling of the atoms.

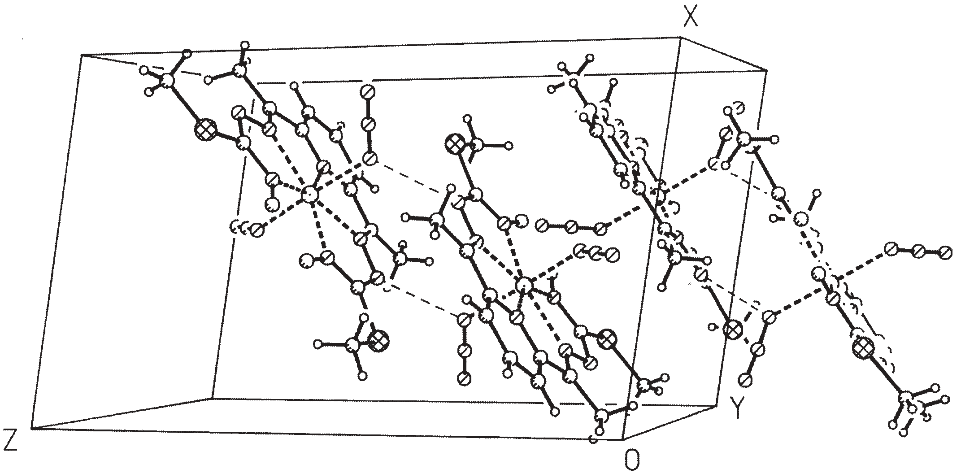

Fig. 3. Packing diagram of the complex molecules viewed along the most representative direction.

The structure was solved by the Patterson methods and refined by full-matrix least squares calculations with all non-hydrogen atoms assigned anisotropic thermal parameters (29 non-H atoms, 264 parameters, $S =$

0.86). The hydrogen atoms bonded to carbon and to N3' were included using a riding model (C–H = 0.096 nm, N–H = 0.090 nm, U(H) = 1.2 times the U_{eq} value of the C or N atom). The H atoms bonded to nitrogens N5' and N5" were refined using a N–H distance restraint of 0.090 nm. The final R value was 0.047 [R_w = 0.048 for a weighting scheme $w^{-1} = \sigma^2(F) + 0.0005 \cdot F^2$] which led to a featureless analysis of variance in terms of sin θ and F_0. The maximal value of Δ/σ = 0.001 and max. and min. heights in the final $\Delta\rho$-map were 380 and 300 $e^{-}nm^{-3}$, respectively. The atomic scattering factors, including correction for anomalous dispersion, were taken from the International Tables for X-ray Crystallography.[13] The final atomic fractional coordinates are given in Table I. The bond distances and bond angles are presented in Table II. A perspective view of the complex molecule with the atomic labeling is shown in Fig. 2, whereas Fig. 3 shows the packing plot diagram of the unit cell.

RESULTS AND DISCUSSION

Synthesis and general physical characteristics of the complex

The title complex [Fe(HL)(N_3)$_2$] was synthesized by the reaction of a methanolic solution of NaN_3 and an unidentified product formed in the template reaction of a methanolic solution of 2,6 diacetylpyridine and S-methylisothiosemicarbazidehydroiodide on the $FeCl_3$ matrix in the presence of LiOAc. The complex contains the monoanionic form of the ligand resulting from deprotonation of the imido-form of one of the two isothiosemicarbazide moieties. The obtained complex is a black crystalline substance stable in air. It is poorly soluble in water and common organic solvents except for DMF. The molar conductivity of a 1×10^{-3} mol dm^{-3} DMF solution is about 8 S cm^2 mol^{-1}, which suggests coordination of both N_3^- ions, even in a solution of such a nucleophilic solvent as DMF. In the IR spectrum of the compound there are characteristic $\nu_a(N_3)$ and $\nu_s(N_3)$ at 2050 and 1340 cm^{-1}, respectively.[14] The effective magnetic moment of the complex has a value μ_{eff} = 5.97 μ_B which corresponds to a high-spin state of iron(III).

Description of the structure

The crystal structure of the title compound consists of discrete [Fe(HL)(N_3)$_2$] molecules bound together *via* hydrogen bonds [N11 – H-N3'(1-X; -Y; -Z) = 0.2887 nm] into the centrosymmetric dimers as shown in Fig. 3. The geometry of the complex molecule (Fig. 2) is characterized by the planar surroundings of the pentadentate (N_5) ligand HL and two monodentate azide groups around the central Fe(III) ion. The coordination polyhedron is essentially a pentagonal-bipyramid, the axial position being occupied by two azide groups, with the pentaaza HL ligand defining the equatorial coordination plane. The coordination polyhedron is slightly deformed in the axial direction: Fe–N11 = 0.2088(5) and Fe–N21 = 0.2066(5) nm, with the angle N11–Fe–N21 being 170.1(2)°. The chelate ligand donor nitrogen–iron distances all lie within the range of 0.2039–0.2269 nm, three of which are longer, belonging to the pyridine and hydrazine nitrogens [Fe–N1 = 0.2232(5), Fe–N2' = 0.2269(5), Fe–N2" = 0.2221(5) nm], while the Fe–N bond distances of the NH terminal group nitrogens are somewhat shorter [Fe–N5' = 0.2167(5) and Fe–N5" = 0.2039(5) nm]. The N_5 donor set of HL, which form a pentagon, are approximately coplanar, the sum of the five angles of the pentagonal girdle being 360.1°. All bond distances and bond angles of the complex molecule exhibit the expected values. Thus, both axial Fe–N(azide) bonds, as is commonly observed for PBP structures,[15] are in average somewhat shorter (0.2077 nm) than the Fe–N equatorial bonds (0.2186 nm). Both azide groups have practically a linear configuration: N11–N12–N13 = 177.6(7)º and N21–N22–N23 = 178.6(5)º with the bond N11–N12 = 0.1192(8) nm, *i.e.*, N21–N22 = 0.1179(6) nm being somewhat longer than N12–N13 = 0.1150(11) nm, *i.e.*, N22–N23 = 0.1157(6) nm, which is in agreement with the literature data.[16,17] The bond distances and bond angles for the once-deprotonated chelate ligand (HL) are in good agreement with the corresponding bond distances and bond angles found in the crystal structure of a Mn(II) complex with neutral chelate ligand (H_2L), of the same type.[9]

TABLE III. Bond angles/º

N(1)-Fe-N(2’)	68.5(2)	N(1)-Fe-N(2”)	69.9(1)
N(2’)-Fe-N(2”)	138.4(1)	N(1)-Fe-N(5’)	138.0(2)
N(2’)-Fe-N(5’)	69.6(1)	N(2”)-Fe-N(5’)	151.7(1)
N(1)-Fe-N(5”)	140.3(2)	N(2’)-Fe-N(5”)	151.1(2)
N(2”)-Fe-N(5”)	70.4(2)	N(5’)-Fe-N(5”)	81.7(2)
N(1)-Fe-N(11)	86.8(2)	N(2’)-Fe-N(11)	84.1(2)
N(2”)-Fe-N(11)	93.5(2)	N(5’)-Fe-N(11)	93.1(2)
N(5”)-Fe-N(11)	93.9(2)	N(1)-Fe-N(21)	84.4(2)
N(2’)-Fe-N(21)	88.3(2)	N(2”)-Fe-N(21)	87.8(2)
N(5’)-Fe-N(21)	90.3(2)	N(5”)-Fe-N(21)	95.8(2)
N(11)-Fe-N(21)	170.1(2)	C(4’)-S(4’)-C(41’)	102.8(3)
C(4”)-S(4”)-C(41”)	103.4(3)	Fe-N(1)-C(2)	120.2(4)
Fe-N(1)-C(6)	119.2(3)	C(2)-N(1)-C(6)	120.5(4)
Fe-N(2’)-N(3’)	116.8(3)	Fe-N(2’)-C(1’)	123.1(4)
N(3’)-N(2’)-C(1’)	120.0(4)	Fe-N(2”)-N3”)	119.5(3)
Fe-N(2”)-C(1”)	122.6(3)	N(3”)-N(2”)-C(1”)	117.7(4)
N(2’)-N(3’)-C(4’)	113.2(4)	N(2”)-N(3”)-C(4”)	106.0(4)
Fe-N(5’)-C(4’)	121.4(3)	Fe-N(5”)-C(4”)	119.6(3)
Fe-N(11)-N(12)	121.3(4)	N(11)-N(12)-N(13)	177.6(7)
Fe-N(21)-N(22)	128.1(4)	N(21)-N(22)-N(23)	178.6(5)
N(1)-C(2)-C(3)	120.1(5)	N(1)-C(2)-C(1’)	115.7(4)
C(3)-C(2)-C(1’)	124.2(4)	C(2)-C(3)-C(4)	119.0(5)
C(3)-C(4)-C(5)	121.2(5)	C(4)-C(5)-C(6)	117.3(5)
C(3)-C(4)-C(5)	121.2(5)	C(4)-C(5)-C(6)	117.3(5)

TABLE III. Continued

N(1)-C(6)-C(5)	121.8(4)	N(1)-C(6)-C(1”)	115.5(4)
C(5)-C(6)-C(1”)	122.7(5)	N(2’)-C(1’)-C(2)	112.4(4)
N(2’)-C(1’)-C(11’)	125.0(5)	C(2)-C(1’)-C(11’)	122.6(4)
N(2”)-C(1”)-C(6)	112.7(5)	N(2”)-C(1”)-C(11”)	124.2(5)
C(6)-C(1”)-C(11”)	123(5)	S(4’)-C(4’)-N(3’)	110.4(4)
S(4’)-C(4’)-N(5’)	130.9(4)	N(3’)-C(4’)-N(5’)	118.7(5)
S(4”)-C(4”)-N(3”)	117.3(4)	S(4”)-C(4”)-N(5”)	118.4(4)
N(3”)-C(4”)-N(5”)	124.3(4)		

There are four five-membered chelate rings all having well localized electronic charge density. The *imido* form of the S-methylisothiosemicarbazide parts of the ligand, which is characteristic for the majority of S-alkyl derivatives of thiosemicarbazides and thiosemicarbazones,[6] has also been confirmed. The electronic charge density is well localized along the N5’–C4’–N3’ and N5”–C4”–N3” fragments, as indicated by the values of the corresponding bond distances (Table II).

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ИЗВОД

КОМПЛЕКСИ ПРЕЛАЗНИХ МЕТАЛА СА ЛИГАНДИМА НА БАЗИ ТИОСЕМИКАРБАЗИДА. ДЕО 45. СИНТЕЗА, КРИСТАЛНА И МОЛЕКУЛСКА СТРУКТУРА [2,6-ДИАЦЕТПИРИДИН bis(S-МЕТИЛИЗОТИОСЕМИКАРБАЗОНАТО)]ГВОЖЂЕ(III)

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Темплатном реакцијом топлог MeOH раствора $FeCl_3 \cdot 6H_2O$, S-метилизотиосемикарбазидхидројодида и 2,6-диацетилпирадина у присуству LiOAc и NaN_3 добијен је високоспински комплекс $[Fe(HL)(N_3)_2]$, где је HL моноанјон bis(S-митилизотиосемикарбазон) 2,6-диацетилпиридина. Рендгеноструктурна анализа комплекса је показала пентагоналну бипирамидалну координацију централног јона Fe(III) са пентадентатним лигандом (HL) у екваторијалној равни и две монодентатне азидне групе у врховима бипирамиде. Кристалографски подаци су: моноклински кристални систем, $P2_1/c$, $a = 1.0263(2)$, $b = 1.2525(2)$, $c = 1.6660(3)$ nm, $\beta = 98.94^\circ$, $V = 2.1154$ nm^3, $Z = 4$, $\rho_x = 1.499$ g cm^{-3}, $\rho_0 = 1.48$ g cm^{-3}.

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