

SYNTHESIS AND STRUCTURE OF COBALT(II) COMPLEX WITH 2,6-DIACETYLPIRIDINE-BIS(PHENYLHYDRAZONE)

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ABSTRACT

The molecular and crystal structure of a newly synthesized Co(II) complex with 2,6-diacetylpyridine bis(phenylhydrazone) (L), of the formula $[\text{CoL}_2]_2$ are described. The reaction of warm EtOH solutions of the ligand, 2,6-diacetylpyridine bis(phenylhydrazone) and CoI_2 in molar ratio 1:1 resulted in formation of black single crystals of the title complex. This is the first and so far, the only metal complex with this ligand that is characterized by single crystal X-ray crystallography. Co(II) is situated in a distorted *mer*-octahedral surrounding of two tridentate N_3 coordinated ligand molecules. Complex crystallizes in monoclinic crystal system in $C2/c$ space group. Besides X-ray analysis, conductometric, spectroscopic and magnetic properties of the complex are investigated.

Keywords: Metal complex, Hydrazone, 2,6-diacetylpyridine derivative, Structure determination.

INTRODUCTION

Hydrazones represent a large and versatile group of organic compounds, characterized by >C=N-N< atomic triade. They are usually prepared by the condensation of carbonyl compounds and hydrazine or its derivatives. Considering the variety of both carbonyl compounds and hydrazine derivatives, the large number of synthesized hydrazones is not surprising. This topic is very interesting for researchers, thus numerous review papers and monographs are published (Guimarães et al., 2017; Kitaev, 1977; Kitaev & Buzykin, 1974; Rollas et al., 2007; Shakhdofa et al., 2014; Watanabe et al., 2018; Yang et al., 2016).

These compounds are important not only from theoretical, but also practical point of view (wide range of biological activity, catalytic activity, use as analytical reagents, etc.) (Guimarães et al., 2017; Rollas et al., 2007; Shakhdofa et al., 2014; Watanabe et al., 2018; Yang et al., 2016).

Having different electron-donor atoms (N, O, S, etc.) to coordinate the metal ions, made this group of compounds very interesting topic for coordination chemists (Kogan et al., 1990; Shakhdofa et al., 2014; Watanabe et al., 2018). Among these ligands, 2,6-diacetylpyridine bis(hydrazones) stand out. These ligands can have different denticity, depending on the hydrazine derivative, but the most common are tri- and pentadentate ones.

The simplest ligand of this group is 2,6-diacetylpyridine bis(hydrazone), which is obtained in the reaction of hydrazine hydrate and 2,6-diacetylpyridine (Shee et al., 2013). This N_3 tridentate ligand coordinates the metal ion through pyridine and two imine nitrogen atoms, forming two 5-membered metallocycles. The only exception is a dimeric complex of Cd(II)

in which, besides the mentioned three ligands, the terminal nitrogen atom is involved in coordination as a bridge (Shee et al., 2013).

In (Curry et al., 1967) synthesis, spectroscopic and magnetic characterization of mono- and bis(ligand) complexes of Fe(II), Co(II), Ni(II) and Cu(II) with 2,6-diacetylpyridine bis(phenylhydrazone) (L), of the general formulas M(L)Cl_2 , and $[\text{ML}_2](\text{ClO}_4)_2$, are described.

The survey of the Cambridge Structural Database (version 5.39, update May 2018) (Groom et al., 2016) revealed that there are no structurally characterized metal complexes with this ligand. Here we report molecular and crystal structure, as well as some physicochemical properties of a novel complex of CoI_2 with 2,6-diacetylpyridine bis(phenylhydrazone), of the formula $[\text{CoL}_2]_2$. This is the first complex of any metal with this ligand, which is obtained in the form of single crystals, thus fully structurally characterized.

EXPERIMENTAL

Materials and methods

All chemicals used were commercial products of analytical reagent grade. Elemental analyses (C, H, N) of air-dried complexes were carried out by standard micromethods in the Center for Instrumental Analyses, ICTM in Belgrade. Molar conductivities of freshly prepared complexes solutions ($c = 1 \times 10^{-3} \text{ mol dm}^{-3}$) were measured on a Jenway 4010 conductivity meter. IR spectra were recorded using KBr pellets on a NEXUS 670 FTIR spectrophotometer (Thermo Nicolet) in the range of $4000\text{--}400 \text{ cm}^{-1}$. Melting points were measured on a Nagema melting point microscope Rapido. Magnetic susceptibility measurements were conducted at room temperature

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on an MSB-MKI magnetic susceptibility balance, Sherwood Scientific Ltd. Cambridge.

Synthesis of ligand

The mixture of 0.80 g (5 mmol) 2,6-diacetylpyridine and 1.45 g (10 mmol) phenylhydrazine-hydrochloride was heated in 10 cm³ EtOH. In the resulting red solution 2.00 g (20 mmol) LiOAc·2H₂O was added and this mixture was refluxed for 40 minutes, during which the solution became yellow. Cooling to the room temperature resulted in the formation of yellowish fibrous product, which was filtered and washed with EtOH and Et₂O. Yield: 1.28 g (75 %). Anal. Calcd. for C₂₁H₂₁N₅: C, 73.44; H, 6.16; N, 20.39. Found: C, 73.54; H, 6.05; N, 20.18. IR bands [$\tilde{\nu}$ /cm⁻¹]: 3432m, 3347m, 1601vs, 1563s, 1508m, 1452s, 1363w, 1291w, 1250vs, 1164vs, 1081w, 994w, 840w, 815w, 750m, 694m, 650w, 507w. M.p. = 216–218 °C.

Synthesis of complex

The mixture of 0.032 g CoI₂ (0.1 mmol) and 0.034 g (0.1 mmol) of L was heated in 10 cm³ of MeOH until complete dissolution. The obtained dark solution was left at the room temperature and after two days black prismatic single crystals were filtered and washed with MeOH. Yield: 0.030 g (60 %). Anal. Calcd. for [C₄₂H₄₂CoN₁₀]₂: C, 50.87; H, 4.11; N, 14.32. Found: C, 50.46; H, 4.23; N, 14.01. IR bands [$\tilde{\nu}$ /cm⁻¹]: 3545m, 3410m, 3160s, 3097m, 3050m, 2980m, 2938m, 1598vs, 1515s, 1494s, 1439m, 1380w, 1261vs, 1170m, 1090m, 1049m, 881w, 804w, 750s, 694s, 662w, 501w. M.p. > 250 °C. Molar conductivity, Λ_M (S cm² mol⁻¹): 150 (MeOH). μ_{eff} (BM): 4.58.

Crystal structure determination

Diffraction experiment was performed on an Oxford Diffraction Gemini S diffractometer, equipped with Sapphire3 detector. The measurements were performed at room temperature. Radiation from sealed tube with Mo-anode was used. Unit cell determination, data collection, and reduction was performed with the *CrysAlisPro* software (Rigaku Corporation, 2015). The crystal structure was solved by using *SHELXT* (Sheldrick, 2015a), and refined by full-matrix least squares method by using *SHELXL-2018* (Sheldrick, 2015b) and *ShelXle* (Hübschle et al., 2011). Software used for crystal structure analysis: *PLATON* (Spek, 2009), *Mercury CSD* (Macrae et al., 2008), and *CrystalExplorer* (Turner et al., 2017).

CCDC 1883840 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

A summary of the crystallographic data for crystal structures is given in Table 1.

Table 1. Crystallographic data and refinement statistics.

Crystal data	
Chemical formula	[C ₄₂ H ₄₂ CoN ₁₀] ₂
M_r (g cm ⁻³)	999.58
Crystal system	Monoclinic
Space group	<i>C2/c</i>
Temperature (K)	294
a (Å)	21.1576(4)
b (Å)	15.8949(3)
c (Å)	12.1287(2)
β (°)	92.247(2)
V (Å ³)	4075.72(13)
Z	4
Crystal size (mm)	0.69 × 0.42 × 0.27
Data collection	
Diffractometer	Gemini S (Oxford Diffraction)
Radiation type	Mo $K\alpha$
No. of measured reflections	17919
No. of independent reflections	4839
No. of observed [$I > 2\sigma(I)$] reflections	4092
R_{int}	0.020
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.678
μ (mm ⁻¹)	1.98
Absorption correction	Analytical
$T_{\text{min}}, T_{\text{max}}$	0.168, 0.467
Refinement	
No. of reflections	4839
No. of parameters	257
No. of restraints	2
H-atom treatment	Mixed
$R[F^2 > 2\sigma(F^2)]$	0.032
$wR(F^2)$	0.079
S	1.05
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.74, -0.71

RESULTS AND DISCUSSION

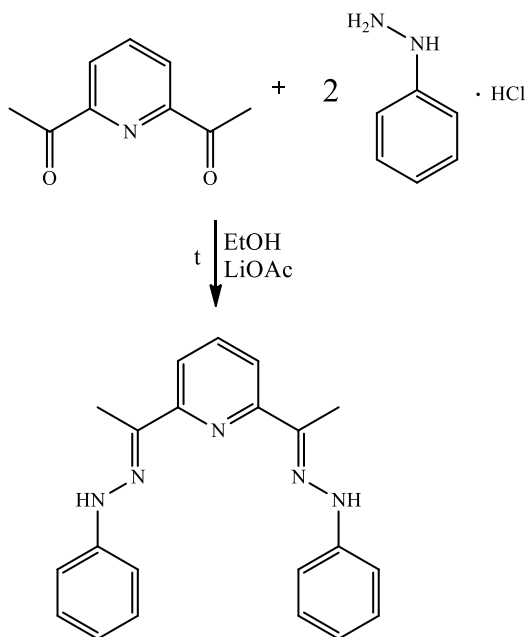
Synthesis and physicochemical characterization of the compounds

Ligand, 2,6-diacetylpyridine bis(phenylhydrazone) is obtained in a good yield (75 %) in the reaction of warm EtOH solutions of stoichiometric amounts of 2,6-diacetylpyridine and phenylhydrazine hydrochloride in the presence of the excess of LiOAc (scheme 1).

It should be mentioned that the same ligand was earlier obtained in the reaction of warm EtOH solutions of 2,6-diacetylpyridine and neutral phenylhydrazine (Curry et al., 1967).

The ligand is well soluble in acetone, partially soluble in MeOH and EtOH, and insoluble in Et₂O and H₂O. Hydrazone structure of the ligand, *i.e.* the condensation of both of keto-groups of the diketone, could be proven by the elemental

analysis, but also the absence of the characteristic very strong carbonyl band at 1707 cm^{-1} in the IR spectrum of the ligand.



Scheme 1. Synthesis of the ligand.

Black single crystals of the complex are obtained in a good yield (60 %) in the reaction of warm EtOH solutions of the ligand and CoI_2 . Despite the fact that metal–ligand molar ratio was 1:1, bis(ligand) complex was formed. Unlike this bis(ligand) complex, in (Curry et al., 1967) the synthesis of mono(ligand) complex of the formula Co(L)Cl_2 is reported. The obtained complex is stable in air and high temperatures (M.p. $> 250\text{ }^\circ\text{C}$), partially soluble in EtOH and H_2O , while its solubility in MeOH

and DMF is better. Molar conductivity of MeOH solution of the complex has a value characteristic for 2:1 electrolyte type, thus is in concordance with the coordination formula (Geary, 1971). The value of the effective magnetic moment ($\mu_{\text{eff}} = 4.58\text{ BM}$) is characteristic for high-spin octahedral Co(II) complexes.

In the IR spectrum of the complex, the band at 3155 cm^{-1} could be ascribed to $\nu(\text{NH})$ vibrations. Other high-energy bands ($3100 - 2940\text{ cm}^{-1}$) correspond to the $\nu(\text{CH})$ vibrations of CH_3 -groups and aromatic rings (pyridine and benzene). Bands at 1599 and 1494 cm^{-1} could be assigned to $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$ vibrations of pyridine and benzene rings, while the band at 1517 cm^{-1} corresponds to $\nu(\text{C}=\text{N})$ vibrations of imine group. In free ligand, the latter is found at higher energy (1563 cm^{-1}), and due to coordination of nitrogen atom suffers a negative shift (Curry et al., 1967; Kazak et al., 2009).

Crystal structure of the complex

The compound crystallizes in monoclinic crystal system, space group $C2/c$. The content of the asymmetric unit, atom numeration, and molecular structure are depicted in Fig. 1. The complex cation exhibits a perfect C_2 symmetry imposed by the space-group symmetry since Co(II) atom occupies a special position. Thus, the asymmetric unit of the unit cell is comprised of a ligand molecule, half of a metal atom, and an iodide ion. The search for higher non-crystallographic symmetry of the complex cation by the method of Continuous Symmetry Measures (Zabrodsky et al., 1992) indicates that cation symmetry only slightly deviates from D_2 point group, as $\text{CSM}(D_2) = 0.251$. Apart from the crystallographic two-fold axis, the two additional non-crystallographic two-fold axes are positioned along N1-Co1-N1^i bonds and the bisector of N2A-N2B^i angle [symmetry code (i): $-x+1, y, -z+1/2$].

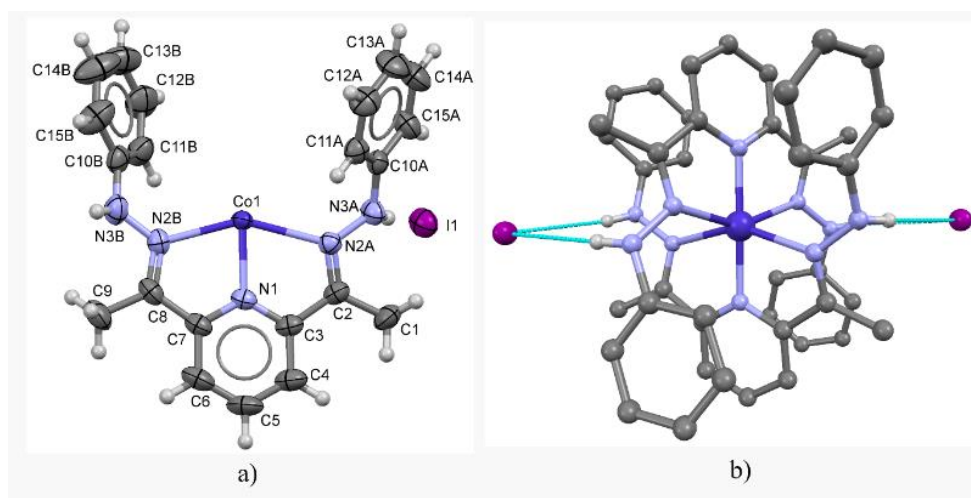


Figure 1. a) Asymmetric unit of $[\text{CoL}_2]\text{I}_2$ and atom labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been drawn as spheres of arbitrary radius. b) Perspective view of the molecular structure of $[\text{CoL}_2]\text{I}_2$.

The Co(II) atom is situated in a distorted octahedral environment, formed by two meridionally arranged tridentate N_3 chelate ligands. The octahedra is distorted, as two ligands are not

mutually perpendicular. The planes defined by N1, N2A and N2B donor atoms of the symmetry-related ligands enclose the dihedral angle of $75.65(6)^\circ$. The valence angles within the

coordination polyhedron deviate from ideal values (Table 2). The *trans*-valence angle N2A–Co1–N2A and *cis*-valence angles N1–Co1–N2A, N1–Co1–N2B with values of 150.69(7)°, 74.14(7)°,

and 76.56(8)°, respectively, display the largest deviations. This is caused by geometry constraints imposed by the ligand structure and its chelate coordination.

Table 2. Selected bond lengths (Å), valence and torsion angles (°).

Bonds	Length (Å)	Bonds	Angle (°)
Co1–N1	2.0061(18)	N1–Co1–N1 ⁱ	173.87(11)
Co1–N2B	2.1993(19)	N2A–Co1–N2B	150.69(7)
Co1–N2A	2.3057(19)	N1–Co1–N2A	74.14(7)
N1–C3	1.338(3)	N1–Co1–N2B	76.56(8)
N1–C7	1.346(3)		
C2–C3	1.467(3)		
C7–C8	1.465(4)		
N2A–C2	1.298(3)		
N2B–C8	1.302(3)		
N2A–N3A	1.374(3)		
N2B–N3B	1.366(3)		
N3A–C10A	1.390(3)		
N3B–C10B	1.400(4)		
		Bonds	Torsion angle (°)
		N1–C3–C2–N2A	16.1(3)
		N1–C7–C8–N2B	4.3(3)
		C2–N2A–N3A–C10A	–161.1(2)
		C8–N2B–N3B–C10B	–165.6(2)

Symmetry code: (i) $-x+1, y, -z+1/2$;

The two five-membered chelate rings are not planar and their conformational analysis is problematic due to large discrepancy between ring bond lengths. The method of Duax et al. (1976) reveals that conformations of these rings are intermediate between the envelope (*E*) and half-chair (*T*) forms. For the Co1–N1–C3–C2–N2A metallocycle, the lowest values of ΔC_s asymmetry parameters are $\Delta C_s(\text{Co1–N1}) = \Delta C_s(\text{C2}) = 6.9(2)^\circ$ and $\Delta C_s(\text{N1–C3}) = \Delta C_s(\text{N2A}) = 9.1(2)^\circ$, which point to 4E and E_5 conformations, respectively. Also, the lowest ΔC_2 asymmetry parameter is $\Delta C_2(\text{C2–N2A}) = \Delta C_2(\text{N1}) = 2.3(2)^\circ$, which suggests 4T_5 conformation. Similarly, for the Co1–N1–C7–C8–N2B ring, the lowest ΔC_s asymmetry parameters $\Delta C_s(\text{C7–C8}) = \Delta C_s(\text{Co1}) = 3.9(3)^\circ$ and $\Delta C_s(\text{N1–C7}) = \Delta C_s(\text{N2B}) = 4.6(2)^\circ$ hint to 1E and E_5

conformations, respectively. Again, the lowest ΔC_2 asymmetry parameter is $\Delta C_2(\text{N2B–Co1}) = \Delta C_2(\text{C7}) = 2.3(2)^\circ$ which signals 1T_5 conformation.

To resolve this ambiguity, a different approach by the method of Cremer & Pople (1975), followed by decomposition of puckering parameters into linear combinations of two basic forms (*E* and *T*) by the method of Evans & Boeyens (1989) was applied. The results are summarized in Table 3. The findings confirm that conformations of both rings are best described as a mixture of half-chair and envelope forms. For the ring Co1–N1–C3–C2–N2A, the conformation is described as 63% E_5 and 37% 4T_5 , while the conformation of ring Co1–N1–C7–C8–N2B is expressed as 57% 1T_5 and 43% E_5 .

Table 3. Cremer–Pople puckering parameters of five-membered rings.

Ring	$Q_2 / \text{Å}$	$\varphi_2 / ^\circ$	$a\varphi(E) + b\varphi(T)^*$
Co1–N1–C3–C2–N2A	0.169(2)	317.3(7)	62.7 (1.8) + 37.3 (1.7)
Co1–N1–C7–C8–N2B	0.1632(18)	349.7(9)	42.8 (2.0) + 57.2 (1.9)

* *a* and *b* are given as percentages. φ is expressed as a multiple of $\pi/2N$.

The ligand is coordinated in a neutral form through nitrogen atoms of the pyridine ring, and two azomethine nitrogen atoms. The same coordination mode is found in $[\text{ZnL}_2](\text{CF}_3\text{O}_3\text{S})_2$, where L is structurally related ligand 2,6-diformylpyridine bis(phenylhydrazone) (Dumitru et al., 2009). Metal–ligand bond lengths are in the range of 2.0061(18)–2.3057(19) Å, with Co–N1 being the shortest one. The two phenylhydrazine moieties are asymmetrically coordinated, as indicated by different metal–ligand bond lengths (Table 2). Intra-ligand bond lengths are in the expected range. The bonds within pyridine and both phenyl rings have lengths indicative of electron delocalization along these moieties. The bonds C2–N2A and C8–N2B are the only two that have lengths characteristic of localized double bonds.

The ligand molecule significantly deviates from planarity. In order to avoid steric clashes with symmetry-related ligand within the coordination polyhedron, a twisting of phenylhydrazine moieties occurs. The magnitude of twisting along C3–C2 bond is greater when compared with that along C7–C8 bond, visualized through the values of torsion angles $\tau(\text{N1–C3–C2–N2A}) = 16.1(3)^\circ$ and $\tau(\text{N1–C7–C8–N2B}) = 4.3(3)^\circ$. The torsion along N2A–N3A and N2B–N3B bonds is similar in magnitude, yet in opposite sense relative to the chelate plane [$\tau(\text{C2–N2A–N3A–C10A}) = -161.1(2)^\circ$, and $\tau(\text{C8–N2B–N3B–C10B}) = -165.6(2)^\circ$]. The mentioned differences between twisting along these bonds lead to significant differences in the final positions of phenyl rings A and B with the respect to the position of the pyridine ring of the symmetry-related ligand

belonging to the same coordination sphere, as it is tabulated in Table 2.

The packing of structural units is dominated by the large complex cation. Cation's Hirshfeld surface (HS) decomposition into intermolecular atom–atom contacts (Fig. 2), reveals that 68.4% of the HS is dominated by cation–cation H···H contacts at distances around or beyond the sum of their Van der Waals radii.

The C···H and H···C contacts comprise 13.2% of the cation's HS. Due to the large discrepancy between cation and anion sizes, only 13.6% of the cation HS can be ascribed to the H···I contacts. However, these contacts correspond to the regions with the lowest d_{norm} values on the cation HS and match NH···I and CH···I hydrogen bonds (Table 4). The anion's HS is over 99% mapped with I···H contacts.

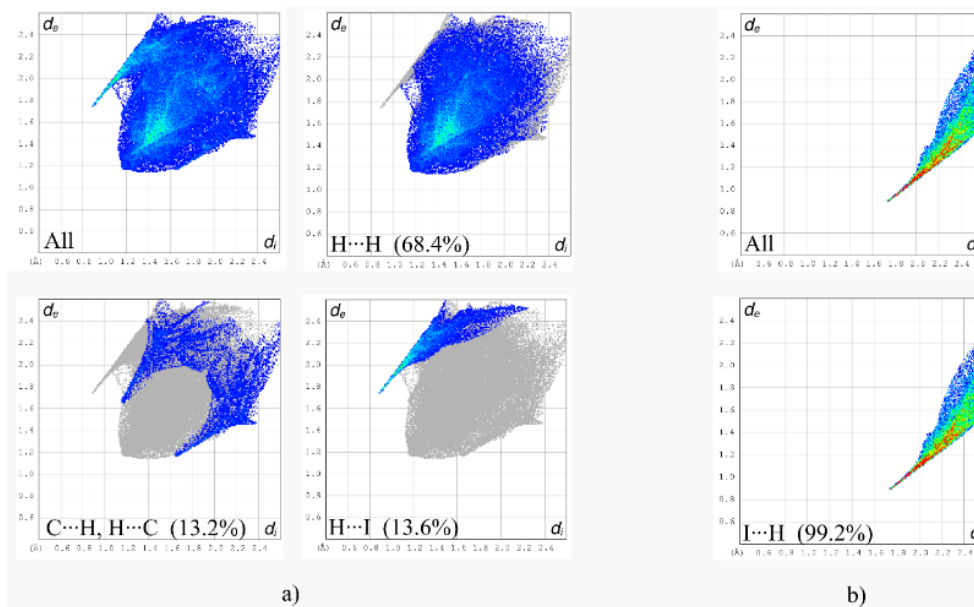


Figure 2. Fingerprint plot of intermolecular contacts, and its decomposition based on specific atom–atom contacts for cation $[\text{CoL}_2]^{2+}$ (a) and anion I^- (b).

Table 4. Selected hydrogen-bond parameters.

$D\text{--}H\cdots A$	$D\text{--}H$ (Å)	$H\cdots A$ (Å)	$D\cdots A$ (Å)	$D\text{--}H\cdots A$ (°)
N3A–H3A···I ⁱ	0.842 (17)	2.802 (18)	3.633 (2)	170 (3)
N3B–H3B···I ⁱ	0.842 (17)	2.87 (2)	3.690 (2)	166 (3)
C1–H1C···I ⁱ	0.96	3.16	3.947 (3)	140.3
C6–H6···I ⁱⁱ	0.93	3.06	3.944 (3)	158.9
C9–H9C···I ⁱ	0.96	3.18	3.927 (3)	136.1

Symmetry code(s): (i) $-x+1, y, -z+1/2$; (ii) $x-1/2, -y+1/2, z-1/2$.

CONCLUSION

By the reaction of warm methanolic solutions of CoI_2 and tridentate N_3 2,6-diacetylpyridine bis(phenylhydrazone), L, not only in molar ratio 1:2, but also in molar ratio 1:1, high-spin bis(ligand) complex of the formula $[\text{CoL}_2]\text{I}_2$ is obtained. Single crystal X-ray analysis has shown that the complex has a distorted *mer*-octahedral configuration. This is the first and so far, the only complex of any metal with the titled ligand, that is characterized by single crystal X-ray analysis.

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