

SYNTHESIS AND CHARACTERIZATION OF COPPER(II) COMPLEX WITH 2,6-DIACETILPYRIDINE-BIS(PHENYLHYDRAZONE)

SVETLANA BELOŠEVIĆ¹, MIRJANA M. RADANOVIĆ^{2*}, MARKO V. RODIĆ², VUKADIN M. LEOVAC²

¹Faculty of Technical Sciences, University of Priština in Kosovska Mitrovica, Serbia

²Faculty of Sciences, University of Novi Sad, Novi Sad, Serbia

ABSTRACT

The syntheses, physicochemical and structural properties of the novel Cu(II) complex with 2,6-diacetylpyridine bis(phenylhydrazone) (L), of the formula $[\text{CuL}_2]\text{Br}_2$ are presented. In the reaction of warm MeOH solutions of the ligand, 2,6-diacetylpyridine bis(phenylhydrazone) and CuBr_2 in molar ratio 2:1 resulted in formation of black single crystals of the bis(ligand) complex. This is the first Cu(II) complex with this ligand that is characterized by SC-XRD. Two ligand molecules are coordinated in the usual tridentate mode, *via* nitrogen atoms of the pyridine ring, and two azomethine nitrogen atoms, forming distorted octahedral environments of the metal ion.

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

INTRODUCTION

For a few decades now, hydrazones are interesting field of research due to their good chelating properties (Kitaev & Buzykin, 1974; Kogan et al., 1990; Watanabe et al., 2018), but the pharmacological activity, as well. The research has shown that some compounds from this group have promising antibacterial, antifungal and antitumor activities (Ainscough et al., 1998; Avaji et al., 2009; Azaz et al., 2007; Mahalingam et al., 2008; Wang et al., 2007), and some of their derivatives are suggested as reagents for the treatment of genetic and neurodegenerative disorders, such as thalassemic syndrome and Alzheimer's (Armstrong et al., 2003; Bernhardt et al., 2007; Buss et al., 2005; Donnelly et al., 2008). Besides, some of these compounds are used as highly sensitive analytical reagents, luminescent probes and molecular sensors (Ávila Terra et al., 2002; Bakir et al., 2008; Basu et al., 2007; Pinto et al., 2004; Sreeja et al., 2003).

2,6-Diacetylpyridine bis(hydrazones) are especially interesting because of their versatile coordination chemistry, i.e., they can act as ligands of different denticity (from tridentate to heptadentate). Even though a large number of metal complexes with this ligand group is synthesized, the number of those that are structurally characterized is rather small (Groom et al., 2016). Since the presence of metal center could often enhance the properties of the organic ligand, even improve its biological activity, it is significant thoroughly to examine the coordination properties of this ligand class, and the structures of the obtained complexes.

Lately, one of these ligands, 2,6-diacetylpyridine bis(phenylhydrazone) (L) became the topic of our research,

thus the crystal structure of the first metal complex, $[\text{CoL}_2]\text{I}_2$, was determined (Belošević et al., 2018). In this paper the synthesis, some physicochemical properties, as well as molecular, and crystal structure of copper complex with the same ligand, of the formula $[\text{CuL}_2]\text{Br}_2$ is reported.

EXPERIMENTAL

Materials and methods

All chemicals used were commercial products of analytical reagent grade, except for the ligand, 2,6-diacetylpyridine-bis(phenylhydrazone), which was synthesized as described previously (Belošević et al., 2018). 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 4000–400 cm^{-1} . Melting points were measured on a Nagema melting point microscope Rapido.

Synthesis of complex

The mixture of 0.024 g CuBr_2 (0.1 mmol) and 0.068 g (0.2 mmol) of L was heated in 5 cm^3 of MeOH until complete dissolution. The obtained dark solution was left at the room temperature and evaporated to a small volume. After 50 h black prismatic single crystals were filtered and washed with MeOH. Yield: 0.033 g (31 %). Anal. Calcd. for $[\text{C}_{42}\text{H}_{42}\text{CuN}_{10}]\text{Br}_2$ (Mr = 910.21): C, 55.42; H, 4.66; N, 15.39. Found: C, 55.98; H, 4.52; N, 15.82. IR bands [$\tilde{\nu} / \text{cm}^{-1}$]: 3440vs, 3157w, 3100w, 2938w, 1634w, 1599s, 1520m,

*Corresponding author: mirjana.lalovic@dh.uns.ac.rs

1494m, 1444w, 1380w, 1264m, 1170w, 1092w, 807w, 750m, 696m, 503w. M.p. = 234 °C. Molar conductivity, Λ_M (S cm² mol⁻¹): 120 (DMF).

Crystal structure determination

Diffraction data were collected on an Oxford Diffraction Gemini S diffractometer equipped with a Sapphire3 CCD area detector. Graphite monochromatized Mo $K\alpha$ radiation was employed. Data reduction was performed with the *CrysAlisPro* software (Rigaku Oxford Diffraction, 2015). The crystal structure was solved by *SHELXT* (Sheldrick, 2015b), and refined with the *SHELXL-2018* (Sheldrick, 2015a). The *ShelXle* (Hübschle et al., 2011) was used as graphical user interface for crystal structure refinement procedures. Additional calculations were performed the *SHAPE* (Llunell et al., 2013) and *CrystalExplorer* (Turner et al., 2017).

CCDC 2059113 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/structures/>.

Table 1. Crystallographic data and refinement statistics.

Crystal data	
Chemical formula	[C ₄₂ H ₄₂ CuN ₁₀]Br ₂
M_r (g cm ⁻³)	910.21
Crystal system	Monoclinic
Space group	<i>C2/c</i>
Temperature (K)	294
<i>a</i> (Å)	20.7769(5)
<i>b</i> (Å)	15.8668(4)
<i>c</i> (Å)	11.8754(3)
β (°)	91.864(2)
<i>V</i> (Å ³)	3912.81(17)
<i>Z</i>	4
Crystal size (mm)	0.50 × 0.31 × 0.19
Data collection	
Diffractometer	Gemini S (Oxford Diffraction)
Radiation type	Mo $K\alpha$
No. of measured reflections	9140
No. of independent reflections	4491
No. of observed [$I > 2\sigma(I)$] reflections	3453
R_{int}	0.021
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.683
μ (mm ⁻¹)	2.646
Absorption correction	Analytical
T_{min}, T_{max}	0.481, 0.693
Refinement	
No. of reflections	4491
No. of parameters	259
No. of restraints	0
H-atom treatment	Mixed
$R[F^2 > 2\sigma(F^2)]$	0.035
$wR(F^2)$	0.088
<i>S</i>	1.03
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.35, -0.66

RESULTS AND DISCUSSION

Synthesis and physicochemical characterization of the complex

The reaction of warm methanolic solution of CuBr₂ and the ligand in molar ratio 1:2 yielded in formation of prismatic single crystals of the complex [CuL₂]Br₂.

The obtained complex is stable in air and high temperatures. It is well soluble in DMF, and partially soluble in alcohols and H₂O. Molar conductivity of its DMF solution has a value characteristic for 2:1 electrolyte type, thus is in concordance with the coordination formula (Geary, 1971).

In the IR spectrum of the complex the band found at 1520 cm⁻¹ could be ascribed to $\nu(C=N)$ vibrations of the imine group. In the spectrum of the ligand, this band is found at higher wavenumbers (1563 cm⁻¹), and due to coordination has suffered a negative shift (Curry et al., 1967; Kazak et al., 2009). The band at 3157 cm⁻¹ corresponds to $\nu(NH)$ vibrations, while the other bands in the range above 2900 cm⁻¹ originate from valent $\nu(CH)$ vibrations of CH₃-groups and aromatic rings (pyridine and benzene). Bands at 1599 and 1494 cm⁻¹ are the result of $\nu(C=C)$, $\nu(C=N)$ vibrations of the mentioned aromatic rings.

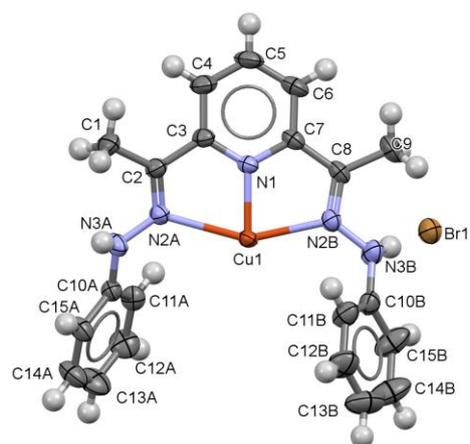
Crystal structure of the complex

The complex [CuL₂]Br₂ is isostructural with [CoL₂]I₂ (Belošević et al., 2018). Both complexes crystallize in *C2/c* space group, with very similar unit cell parameters. Complex cation [CuL₂]²⁺ is situated on a two-fold rotation axis, so that the asymmetric unit of the unit cell is comprised of a ligand molecule, half of a copper atom, and a bromide ion (Figure 1). To facilitate structural comparisons of [CuL₂]Br₂ and [CoL₂]I₂, pertinent structural parameters of both complexes are listed in Table 2. Coordination environment around Cu(II) is heavily distorted, and calculation of continuous shape measure (*CShM*) assigned the coordination polyhedron as heavily distorted octahedron, with *CShM(OC-6)*=5.911 (Alvarez et al., 2005). The coordination environment is formed by two meridionally arranged tridentate N₃ chelate ligands. Dihedral angle enclosed by planes through N1, N2A and N2B donor atoms of the symmetry-related ligands amounts 74.2°. Distortion of the octahedron may be seen through valence angles centered on Cu(II) atom, all of which deviate from ideal values. The largest deviations are observed by The *trans*-valence angle N2A–Cu1–N2A and *cis*-valence angles N1–Cu1–N2A, N1–Cu1–N2B with values of 150.69(7)°, 74.14(7)°, and 76.56(8)°, respectively.

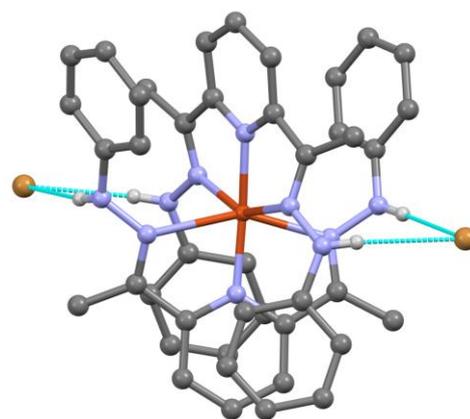
The coordination mode of the ligand, through nitrogen atoms of the pyridine ring, and two azomethine nitrogen atoms, is identical to that found in [CoL₂]I₂ (Belošević et al., 2018), and [ZnL'₂](CF₃O₃S)₂, where L' is structurally related ligand 2,6-diformylpyridine bis(phenylhydrazone) (Dumitru et al., 2009).

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

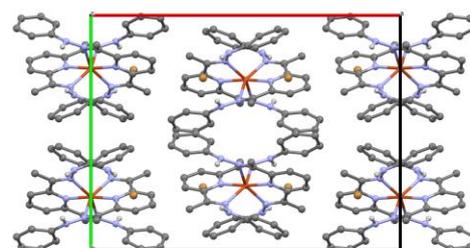
Bonds	[CuL ₂]Br ₂	[CoL ₂]I ₂
	Length (Å)	
M–N1	1.9451(18)	2.0061(18)
M–N2B	2.2170(18)	2.1993(19)
M–N2A	2.3736(18)	2.3057(19)
N1–C3	1.346(3)	1.338(3)
N1–C7	1.357(3)	1.346(3)
C2–C3	1.469(3)	1.467(3)
C7–C8	1.468(3)	1.465(4)
N2A–C2	1.292(3)	1.298(3)
N2B–C8	1.291(3)	1.302(3)
N2A–N3A	1.373(3)	1.374(3)
N2B–N3B	1.369(3)	1.366(3)
N3A–C10A	1.388(3)	1.390(3)
N3B–C10B	1.395(3)	1.400(4)
Bonds	Angle (°)	
N1–Cu1–N1 ¹	173.87(11)	173.26(10)
N2A–Cu1–N2B	150.69(7)	152.17(7)
N1–Cu1–N2A	74.14(7)	74.69(7)
N1–Cu1–N2B	76.56(8)	77.51(7)



a)



b)



c)

Figure 1. Asymmetric unit (a) and formula unit (b) of [CoL₂]I₂; c) Crystal packing viewed along crystallographic *c* axis (hydrogen atoms are omitted for clarity).

CONCLUSION

In this paper synthesis, structure, and some physicochemical properties of the novel complex with 2,6-diacetylpyridine bis(phenylhydrazone), of the formula [CuL₂]Br₂, are described. This is only the second structurally

Metal–ligand bond lengths are in the range of 1.9451(18)–2.3736(18) Å, with Co–N1 being the shortest one. Also, the two phenylhydrazine moieties are asymmetrically coordinated, as indicated by different metal–ligand bond lengths (Table 2). These structural features are analogous to those found in [CoL₂]I₂. Intra-ligand bond lengths and comparable to those found in [CoL₂]I₂. Intra-ligand bonds with localized double character are N2–C2 and N2–C8, while others are in the expected range for *sp*² hybridized atoms, with considerable electron delocalization.

Crystal packing in [CuL₂]Br₂ (Figure 1c) is congruent to that of [CoL₂]I₂. Its investigation by method of Hirshfeld surface (HS) analysis documents striking similarity between [CuL₂]Br₂ and [CoL₂]I₂. Namely, cations HS decomposition into atom-specific contacts (Fig. 2), reveals following distribution: 68.2% of H···H contacts (68.4% for [CoL₂]I₂), 13.7% of C···H or H···C contacts (13.2% for [CoL₂]I₂), and 13.5 of H···I contacts (13.6% for [CoL₂]I₂). As expected, and analogous with results for [CoL₂]I₂, the anion's HS is 99.6% mapped with Br···H contacts.

The bromide ion is involved in two hydrogen bonds, with very similar geometry (Table 3).

Table 3. Selected hydrogen-bond parameters.

<i>D</i> –H··· <i>A</i>	<i>D</i> –H (Å)	H··· <i>A</i> (Å)	<i>D</i> ··· <i>A</i> (Å)	<i>D</i> –H··· <i>A</i> (°)
N3A–H3A···Br1 ¹	0.81(3)	2.64(3)	3.440(2)	168(3)
N3B–H3B···Br1	0.82(3)	2.64(3)	3.456(2)	169(3)

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

characterized metal complex with this ligand, and since this class of compounds is promising from the many point of views it is of a high importance to make some further research in this field.

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