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Synthesis, structural, spectral characterization, DFT analysis and antimicrobial studies of aquabis(L-ornithine)copper(II) picrate

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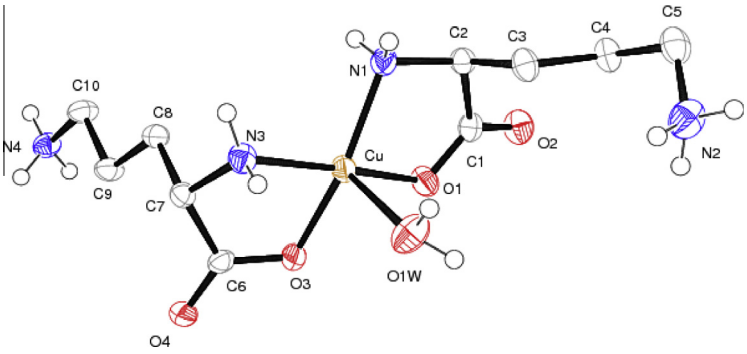
HIGHLIGHTS

- Preparation and characterization of aquabis(L-ornithine)copper(II) picrate.
- Crystal data showed a distorted square-pyramidal geometry for studied complex.
- Complex exhibits antimicrobial activities against Gram-positive and Gram-negative bacteria.
- DFT/B3LYP level is capable to provide satisfactory results for predicting optimized geometry and vibrational data.

GRAPHICAL ABSTRACT



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ABSTRACT

The present work consists of synthesis, spectroscopic, DFT studies and crystal structure investigation of complex $[Cu(L\text{-orn})_2(H_2O)](PIC)_2$ (where L-orn = L-ornithine, PIC = picrate anion). The molecular structure of complex was determined by X-ray crystallography and refined by three-dimensional least squares techniques. Copper atom is five coordinate and two molecules of L-ornithine are coordinating with it through their carboxylate oxygens and amine nitrogens whereas the fifth site is occupied by water molecule. Both of the picrate anions are present outside the coordination sphere of metal ion resulting in formation of charge-separated type complex. EPR spectrum suggests about the distorted square-pyramidal geometry of the complex and is confirmed by X-ray crystallography. The optimized structure of the present complex has been studied using the DFT/B3LYP/6-31G*(d,p)/LANL2DZ level of theory. The vibrational assignments and HOMO–LUMO were theoretically examined by means of the hybrid DFT method. Also the antimicrobial properties of the title complex have been explored in the present work.

Introduction

Copper is a constituent of many enzymes that act as catalysts for a number of biochemical reactions. Presence of a small amount of copper is essential and beneficial whereas its excess causes toxicity and may produce lethal effects in all living organisms. For the last few decades, complexes of Cu(II) with amino acids have attracted a lot of attention. There are several evidences available of their involvement in various physiological processes. Copper-histidine complex is useful in the treatment of Menkes disease [1]. The complexes of Cu(II) with L-proline, L-leucine/isoleucine

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and L-ornithine in the presence of heterocyclic bases have shown DNA binding and oxidative cleavage activity. These also have the potential for cellular applications in chemotherapeutic agents. Efficient chemical nuclease activity was shown by copper(II) complexes of L-lysine [2]. Transition metal complexes of amino acids have a significant role in cancer chemotherapy. Mixed ligand complexes involving asparagine in combination with various metal ions have been suggested as possible antimetabolites in tumor cells [3]. Complexes of transition metals with amino acids in proteins and peptides are utilized in numerous biological processes like electron transfer, oxidation and as oxygen conveyers. In these processes, the enzymatic active site, which is very specific, forms complexes with divalent metal ions [4].

L-ornithine is one of the four important amino acids having basic side chains, although it is not a constituent of proteins. L-ornithine is effective for stimulating, production and release of growth harmones and reducing hypertension [5]. Its function in the living systems is very important because of its role in Krebs cycle in the metabolism of mammals [6]. In the rapidly growing tumors, there is decarboxylase activity, and it can be reduced by chelating the carboxylate group of ornithine [5]. Potential medical uses of ornithine are, its antifatigue effect, cirrhosis and as weight lifting supplement [7].

Earlier X-ray diffraction technique was used to determine the structure of the cupric complex of ornithine with two chloride ions as counter anions. In this complex both the counter anions and solvent molecules are present outside the coordination sphere of metal ion and adopt square planar geometry [8]. In the previously reported work, [Cu(L-ornithine(phen)(Cl)]Cl.2H_2O complex, the square-pyramidal geometry was acquired by the metal atom with coordination number 5 in the presence of chloride as counter anion. In this complex, Cu(II) coordinates with two nitrogen atoms of 1,10-phenanthroline, one nitrogen atom of an amino group, one carboxylate oxygen atom of L-ornithine in the equatorial positions and Cl^- at the elongated apical position. Two water molecules present outside the coordination sphere [2c]. Here, we have presented the crystal and molecular structure of cupric complex of L-ornithine in the presence of picrate as counter anions. The structure is solved to elucidate the influence of counter anions and solvent on the bonding and the geometry of the metal ions. The presence of electron-withdrawing group of the picrate ion makes it good pi-acceptor for cations as well as neutral carrier donor molecules [9].

Experimental

Material and instrumentation

All chemicals, solvents used in this study were of high purity. L-ornithine was supplied by Loba Chemie and used without purification. Picric acid was used after recrystallization. The IR absorption spectrum of the complex was recorded in the range of 450–4000 cm^{-1} by means of a Perkin Elemer FTIR RX I spectrometer with KBr pellets (Sigma Aldrich). The elemental analyses was performed on Flash 2000 Organic Elemental Analyzer. EPR measurement was carried out at room temperature using a Bruker EMX EPR spectrometer. For antimicrobial activity, pathogenic bacteria *Serratia marcescens* (MTCC-97), *Sphingobium japonicum* (MTCC-6362), *Stenotrophomonas maltophilia* (MTCC- 2446) and *Staphylococcus aureus* (MTCC-3160) were procured from Microbial Type Culture Collection (MTCC), Institute of Microbial Technology, Chandigarh.

X-ray diffraction

X-ray diffraction data was collected with "Bruker APEX-II CCD" area detector diffractometer with graphite monochromated Mo Kα radiation (λ = 0.7107 Å) source. The crystal structure was calculated by the direct method using the program SIR-97 [10] and refinement was performed using full-matrix least-squares methods SHELXL-97 programme. Absorption corrections were carried out using the multi-scan program [11]. The hydrogen atoms of methylene group, terminal and α-amino groups were located from the difference

Fourier map and refined isotropically. Molecular drawing of the complex was obtained with the help of ORTEP [12] and MERCURY programme [13]. H-bonding was calculated by using PARST [14]. The crystallographic data for the complex is summarized in Table 1.

Synthesis

Copper(II) picrate was prepared by the reaction of copper carbonate with picric acid (1:2) in aqueous medium. The solution was stirred for 1 h at 40 °C on a magnetic stirrer. Green color crystals of copper(II) picrate were obtained on concentrating the reaction mixture. The present complex [Cu(L-orn)$_2$(H_2O)](PIC)$_2$ was synthesized by dissolving Cu(II) picrate and ornithine (1:2) in an aqueous solution. The mixture was stirred for 1 h at 50 °C and then left to cool down at room temperature. Change in color of the solution confirms the completion of reaction. Slow evaporation of the solution yielded dark green color crystals after 72 h. The melting point of the crystals was found to be 165 °C. Yield: 80%. IR (KBr) cm^{-1}: 3421 (ν (OH) br), 3238 (ν_s (NH_2, vs)), 3145 (ν_{as} (NH_3^+, s), 2957 (ν (C—H) br), 1632 (ν (C=O), vs), 1370 (ν (C—O), m) 1563 (ν_{as} (NO_2), s), 1335 (ν_s (NO_2), vs). Elemental Analysis: Anal. Calc. for $C_{22}H_{30}CuN_8O_{19}$: C, 32.94%; H, 3.54%; N, 17.51%. Found: C, 33.00%; H, 3.48%; N, 17.49%.

Theoretical calculations

In the present investigation, geometry optimization of the title complex was carried out using the B3LYP/6-31G*(d,p)/LANL2DZ level of theory. 6-31G (d,p) is a popular polarized basis set which

Table 1
Crystallographic data for complex [Cu(L-orn)$_2$(H_2O)](PIC)$_2$.

Compound	[Cu(L-orn)$_2$(H_2O)](PIC)$_2$
Empirical formula	C_{22} H_{30}Cu N_{10} O_{19}
Formula weight	802.11
Crystal system	Orthorhombic
Crystal size	0.13 × 0.11 × 0.09
Color	Green
Shape	Rectangular
Space group	P 2_1 2_1 2_1
Unit cell dimensions (Å), (°)	a = 7.816 (4) α = 90.000 b = 14.506 (8) β = 90.000 c = 27.880(14) γ = 90.000
Volume (Å^3), Z	3161(3), 4
ρ_{calc} (g cm^{-3})	1.686
μ (cm^{-1})	0.793
F (000)	1652.0
Range of data collection	1.46–32.38
Limiting frequency	$-11 \leqslant h \leqslant 8$ $-21 \leqslant k \leqslant 21$ $-41 \leqslant l \leqslant 39$
Total reflections	27153
Independent reflections	11286 [R(int) = 0.0280]
Completeness to theta = 25.00	99.8%
Refinement method	Full matrix least squares on F^2
Data/restraints/parameters	11286/12/505
Goodness of fit on F^2	1.033
Final R indices [I > 2 (I)]	$R1$ = 0.0533, w$R2$ = 0.1439
R indices (all data)	$R1$ = 0.0668, w$R2$ = 0.1529
Largest diff. peak & hole (e Å^3)	1.029 and −0.825
Deposition number	CCDC 894386

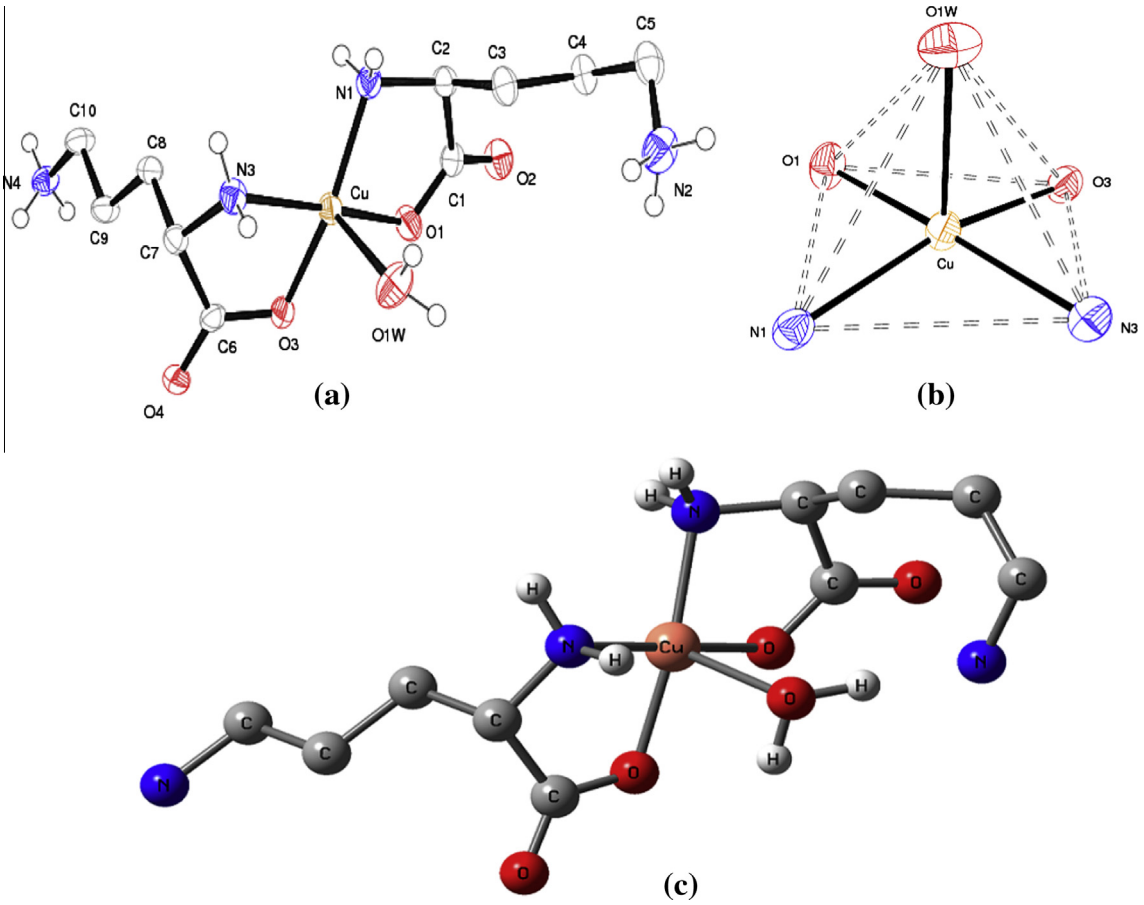

Fig. 1. (a) ORTEP diagram of the complex with atom labeling scheme. Picrate anions and hydrogen atoms have been removed for clarity, (b) distorted square-pyramidal view of the complex and (c) optimized structure of the complex using the B3LYP/6-31G*/LANL2DZ level of theory.

Table 2
Selected geometric parameters from X-ray and DFT-B3LYP calculations for $[Cu(L\text{-orn})_2(H_2O)](PIC)_2$.

Bond distances (Å)	Experimental	Theoretical	Deviation
Cu—N1	2.002 (2)	2.093	−0.091
Cu—N3	2.000 (2)	2.064	−0.064
Cu—O1	1.951 (19)	1.975	−0.024
Cu—O3	1.955 (18)	1.980	−0.025
Cu—O1 W	2.280 (2)	2.307	−0.027
Bond angles (°)			
N1—Cu—N3	100.26 (9)	100.68	−0.42
N1—Cu—O1	83.66 (8)	79.59	4.07
N1—Cu—O3	158.64(9)	169.59	−10.95
N3—Cu—O1	169.97 (9)	179.41	−9.44
N3—Cu—O3	83.63 (8)	81.16	2.47
N1—Cu—O1W	103.26 (10)	107.99	−4.73

adds *p* functions to hydrogen atoms in addition to the d functions on heavy atoms, while LANL2DZ is a basis set for post-third row atoms. The comparison of data obtained from theoretically optimized structure and crystallographic determined structure was carried out. All the DFT calculations were performed by using Gaussian 03 program on a personal computer and Gauss View was used for visualization of the structure, simulated vibrational spectra and molecular orbitals [15–18]. HOMO and LUMO analysis have been used to elucidate the information regarding the charge transfer within the molecule. These calculations are valuable for providing insight into the vibrational spectrum and molecular parameters like bond distances and bond angles.

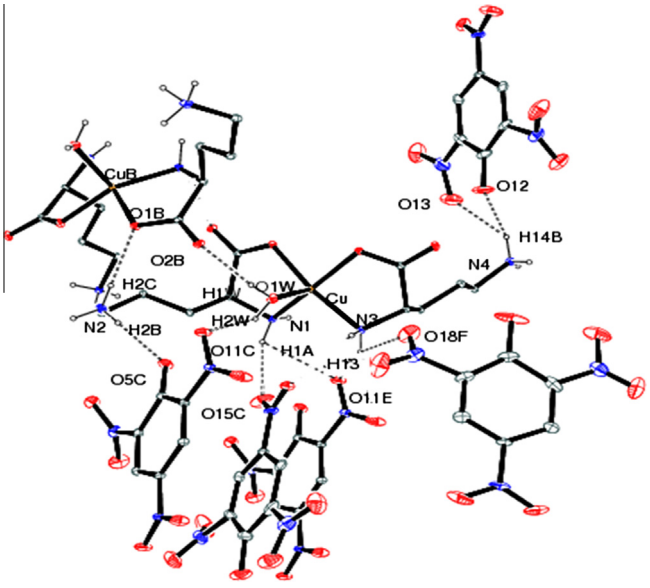

Fig. 2. Molecular structure of the complex with hydrogen bonding interactions.

Antimicrobial activity

The antimicrobial activities of picric acid (PIC), copper(II) picrate and the present complex $[Cu(L\text{-orn})_2(H_2O)](PIC)_2$ were tested against pathogenic Gram −ve (*S. marcescens*, *S. japonicum*, *S.*

maltophilia) and Gram +ve (*S. aureus*) bacterial strains using the broth microdilution method. The procedure to carry out the minimum inhibitory concentration of the metal complexes was described earlier in the copper(II) and silver(I)picrate complexes [19]. The antimicrobial activities of metal complexes were evaluated as minimum inhibitory concentration where no viability of bacteria was observed after incubation of 48 h.

Results and discussion

Description of the crystal structure

The crystal structure of the complex $[Cu(L\text{-orn})_2(H_2O)](PIC)_2$ was determined by a single crystal X-ray diffraction method. The molecular structure of the copper complex is shown in Fig. 1a. It crystallized in the orthorhombic $P2_1\ 2_1\ 2_1$ space group and is similar in many ways of other Cu(II) complexes of amino acids whose crystal structure have already determined [2]. The geometry around Cu(II) can be best described as distorted square-pyramidal based on structural parameter ($\tau = 0.18$) for five-coordinate molecules. The axial position around the metal ion is occupied by water molecule whereas basal positions are occupied by an α-amino nitrogen and a carboxyl oxygen of each of the two symmetrically related bidentate ornithine ligand. The metal-axial ligand (water) bond length is larger than metal-basal (ornithine) distance (Table 2). Both of the picrate anions remain outside the coordination sphere of the metal ion and are interacting with carboxylate oxygens, nitrogen atoms of terminal and α-amino group through hydrogen bonding interactions. The selected bond lengths and angles are summarized in Table 2.

The terminal as well as α-amino group, carboxylate oxygens and water molecules are involved in extensive hydrogen bonding interactions in 3-dimensional network. Amino groups are donating hydrogen bonds to one of the carboxylate oxygens, phenolic oxygens and oxygen of the o-nitro group of picrate anion in an intermolecular way. Intramolecular hydrogen bonding interactions have also been observed between terminal amino group and phenolic oxygen. Water molecules are donors of hydrogen bonds to carboxylate oxygen and oxygen of the p-nitro group of picrate anion of neighbouring units (Fig. 2, Table 3).

Theoretical calculations

The ground-state structure of the studied complex has been carefully optimized using the B3LYP/6-31G*/LANL2DZ level of theory as shown in Fig. 1c. The copper atom is five coordinate with distorted square-pyramidal geometry. The optimized structural data is in well consistence with the X-ray crystal structure data. As shown in Table 2, the bond lengths and bond angles calculated by the DFT studies are in good agreement with that obtained from crystal structure data. The maximum deviation of bond length 0.091 (Å) for Cu—N1 and of bond angle is 10.95° for N1—Cu—O3.

The characteristic vibrational bands of complex are presented in Table 4. The vibrational bands at 3238 cm^{-1} and 3053 cm^{-1} belong to $\nu_s(NH_2)$ and ($\nu_{as}(NH_3^+)$) and the corresponding signals appear at 3422 cm^{-1} and 3434 cm^{-1} in the theoretical IR spectrum. The appearance of signals at 1632 cm^{-1} and 1370 cm^{-1} correspond to the coordinating (ν (C═O) with Cu(II) ion) and non-coordinating part of (ν (C—O)) stretching bands. The latter is hydrogen bonded either with the water molecule or the neighbouring molecule. The assignments of the vibrational bands at 3421 cm^{-1} belonging to the ν (OH) stretching vibrations while theoretical calculation shows the corresponding bands at 3533 cm^{-1} that suggest the presence of water molecule in the complex [20]. The strong bands in the frequency range 1563 cm^{-1} and 1335 cm^{-1} for the complex correspond to the asymmetric and symmetric stretching of the NO_2 group of picrate anions (Fig. S1), respectively while theoretically calculated vibration bands appear at 1557 cm^{-1} and 1338 cm^{-1}.

The total energy, energy gap and dipole moment have an influence on the stability of molecule. The frontier orbitals HOMO and LUMO are very important parameters for chemical reaction and take part in chemical stability [21]. The transitions can be described from HOMO to LUMO which determine the way in which one molecule interacts with other species. It also determines the molecular electron transport properties because it is a measure of electron conductivity also. In the present complex, the highest occupied molecular orbital (HOMO) is localized over the terminal amino group whereas LUMO is most distributed over the metal

Table 3
Selected hydrogen bonding interactions in $[Cu(L\text{-orn})_2(H_2O)](PIC)_2$ complex.

Hydrogen bonding geometry				
D–H…A	d(D–H)	d(H–A)	d(D–A)	∠(DHA)
N1—H1B…O11E	0.87	2.630	3.015 (4)	107.96
N2—H2C…O1B	0.87	2.091	2.940(3)	163.60
N2—H2B…O5C	0.89	1.960	2.790(4)	153.52
N3—H13A…O18F	0.82	2.513	2.513 (4)	121.33
N4—H14A…O4G	0.84	2.023	2.862(3)	178.40
N4—H14B…O12	0.86	1.987	2.766(6)	149.92
N4—H14B…O13	0.86	2.542	3.139(8)′	127.23
O1W—H1W…O2B	0.83	2.020	2.839 (4)	166.29
O1W—H2W…O11C	0.83	2.760	3.261 (4)	120.56
O1W—H2W …O15D	0.83	2.368	2.890 (4)	121.54

Table 4
Selected experimental and theoretical IR frequencies of $[Cu(L\text{-orn})_2(H_2O)](PIC)_2$ complex.

Assignment	Experimental	Theoretical
ν_s (NH_2), ν_{as} (NH_3^+)	3238 vs 3145 s	3422, 3434
ν (C═O)	1632 vs	1626
ν (C—O)	1370 m	1369
ν (OH)	3421 br	3533
ν (C—H)	2957 br	2966
ν_{as} (NO_2)	1563 s	1557
ν_s (NO_2)	1335 vs	1338

br = Broad, m = medium; s = strong; vs = very strong.

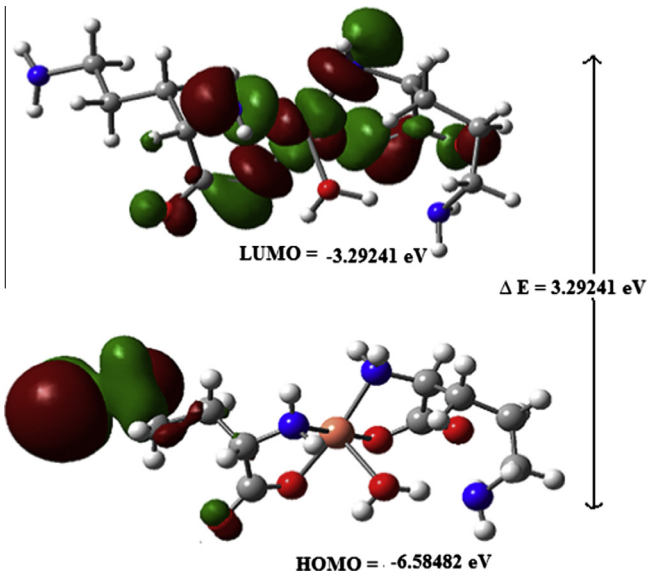

Fig. 3. Atomic orbital compositions of the frontier molecular orbital for complex.

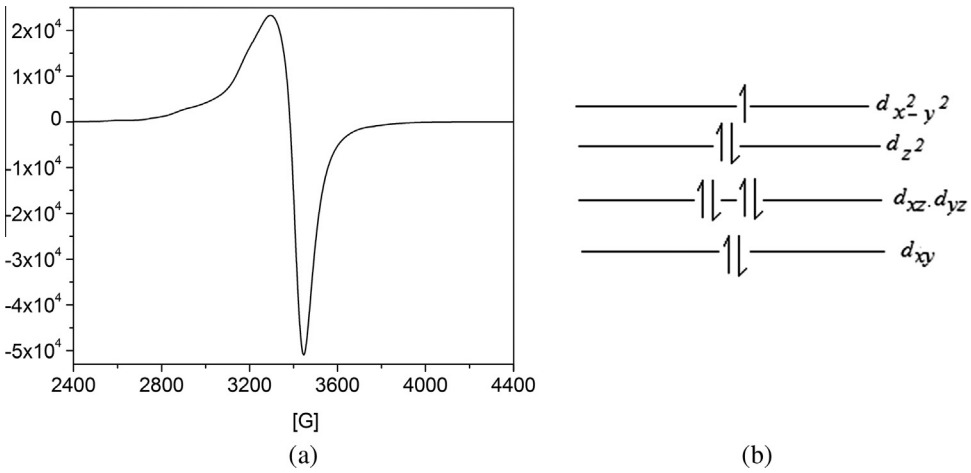

Fig. 4. (a) EPR spectrum of copper complex and (b) a probable splitting pattern for the d orbitals in a square-pyramidal complex.

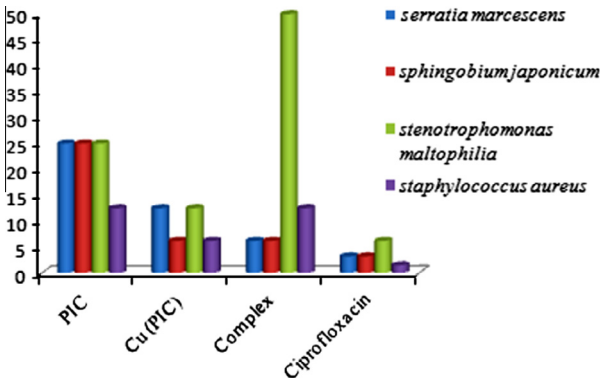

Fig. 5. Antimicrobial activity of the picric acid, metal salt and complex with minimum inhibitory concentration (MIC) in (μg/ml).

center (Fig. 3). Lower HOMO–LUMO energy gap confirms the charge transfer takes place within the complex.

EPR spectral study

The EPR spectrum of the copper complex was recorded at room temperature on X-band frequency of 9.86 GHz under the magnetic field strength varying from 2400 to 4400 G. Intense absorption signal appeared in the high field at 3400 G (Fig 4a). As is apparent in the spectrum of copper complex, g_{II} (2.23) > $g_{\perp}$(2.07) indicating that the unpaired electron is in $d_{x^2-y^2}$ orbital (Fig. 4b) of square pyramidal complexes [22]. The anisotropy in g indicates the presence of a fairly large component of low symmetry in the ligand field.

Antimicrobial activity

The antimicrobial activity of picric acid, copper(II) picrate and synthesized complex $[Cu(L\text{-orn})_2(H_2O)](PIC)_2$ was screened against a panel of pathogenic bacterial strains using the microbroth dilution method. Compounds with α-amino acids like L-ornithine containing terminal amine moiety easily penetrate through cell walls due to their ionic character [5]. The antimicrobial screening data indicate that the metal salt, free acid as well as the complex are displaying fairly good antimicrobial activity against all the four mentioned bacteria. The complex is most effective antimicrobial agent against *S. marcescens* and *S. japonicum* bacterial strains (Fig. 5). MIC values (μg/ml) for the metal salt and its complex with L-ornithine were summarized in Table 5. The amino acid complex was active against bacteria under very low concentration, and minimizing the possible toxic effects.

Conclusion

The copper amino acid complex $[Cu(L\text{-orn})_2(H_2O)](PIC)_2$ was prepared and structurally characterized as charge-separated complex. The coordination number of metal ion is five, having distorted square - pyramidal geometry. An EPR study suggests that the unpaired electron is present in $d_{x^2-y^2}$ orbital indicating distorted square-pyramidal geometry of the complex. Comparison between the experimental and theoretical results indicates that density functional B3LYP/6-31G*/LanL2DZ method is able to provide satisfactory results for predicting structural parameters and vibrational wavenumbers. HOMO–LUMO energy gap suggests the charge-transfer interactions taking place within the complex. The antimicrobial results show that complex has good inhibitory effect without causing any toxicity against all four bacterial strains but it is most effective antimicrobial agent against *S. marcescens* than metal salt and free picric acid.

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Table 5
Minimum inhibitory concentrations for the picric acid, metal salt and complex on bacterial strains by microbroth dilution method (μg/ml).

Complexes	*Serratia marcescens*	*Sphingobium japonicum*	*Stenotrophomonas maltophilia*	*Staphylococcus aureus*
PIC	25	25	25	12.5
Cu (PIC)	12.5	6.2	12.5	6.2
Complex	6.2	6.2	50	12.5
Ciprofloxacin	3.2	3.2	6.2	1.5

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2014.06.061.

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