

## Synthesis and characterization of transition metal complexes with hydrazone ligand

Rohit Kumar Chaurasiya<sup>a</sup>, Sampat Prasad Rawat<sup>b</sup>,  
Genda Lal Prajapati<sup>a</sup> and Ajay Kumar Kamat<sup>a</sup>

<sup>a</sup>Department of Chemistry, A.P.S. University, Rewa (M.P.)

<sup>b</sup>Department of Chemistry, Govt. Vivekanand PG College, Maihar, Satna (M.P.)

Email id : rohitaurasiya012@gmail.com

*Manuscript received online 05 January 2023, accepted on 11 February 2023*

**Abstract :** To synthesized and characterization of a few hydrazones and characterization of metal complexes derived from 2- hydroxypropiophenone nicotinic hydrazone, 2-benzoylpyridine benzoyl hydrazone and di-2-pyridyl ketone nicotinoyl-hydrazone. Here two ligands are NNO donor ligands and the other is an ONO donor ligand. Di-2-pyridyl ketone was selected as the carbonyl part in one of the hydrazone since it can provide a further binding site for metal cation and can thus increase the denticity. There is various physicochemical techniques are use to synthesize the coppe(II) complexes.

**(Keywords):**Hydrazone ligands, copper(II) complexes, UV-vis., EPR)

### Introduction

The architectural beauty of coordination complexes arises due to the interesting ligand systems containing different donor sites in heterocyclic rings e.g.: NNO or NNS. Among the ligand systems, hydrazide and hydrazone occupy special place because transition metal complexes of these compounds

are nowadays extensively used for the treatment of several diseases, in synthetic and analytical chemistry as novel heterogeneous catalysts in oxido- reduction processes and various chemical and photochemical reactions as well as numerous industrial applications of science and technology <sup>1-5</sup>.

In hydrazones, it is well known that a proton transfer can occur between the hydrazinic-N and keto group of hydrazone part. Therefore tautomerization equilibrium exists between amido form and iminol form through intramolecular proton transfer. This proton transfer causes a change in the  $\pi$ -electron configuration and thus increases conjugation. Thus coordination compounds derived from hydrazones contain either neutral amido form or deprotonated form. In solid state, hydrazones predominantly exist in amido form (I), whereas in solution iminol form (II) predominates (Fig 1). This is well established from crystal structures and IR spectral studies.

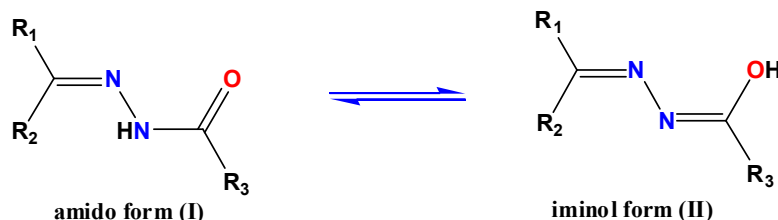


Fig 1. Tautomerism in acylhydrazones

Hydrazones have been intensively investigated mostly because of their potential application as anticancer, antiviral, antibacterial and antifungal agents. These compounds display a versatile behavior in metal coordination and the biological activity is often increased by bonding to transition metals. The current work deals with the synthesis and characterization of a few hydrazones and characterization of metal complexes derived from 2- hydroxy-propioophenone nicotinic hydrazone, 2-benzoylpyridine benzoyl hydrazone and di-2-pyridyl ketone nicotinoylhydrazone. Here two ligands are NNO donor ligands and the other is an ONO donor ligand. Di-2-pyridyl ketone was selected as the carbonyl part in one of the hydrazone since it can provide a further binding site for metal cation and can thus increase the denticity. The choice of nicotinoylhydrazide as the hydrazide part was based on the fact that the nitrogen present in the ring can coordinate to metal center and is capable of forming polymeric structures, even though this type of complexes are not observed in this work.

### Material and methods

#### Physical measurements

The physicochemical techniques carried out for the present investigation are discussed below:

#### Elemental analyses

C, H and N analyses of the ligand and the complexes were performed on a Vario EL III CHNS analyzer at SAIF, Kochi, India. The metal content of the complexes were determined by AAS after digestion with con.  $\text{HNO}_3$ . The analysis were done using Thermo Electron Corporation, M series Atomic Absorption Spectrophotometer at Mar Thoma College, Tiruvalla.

#### Conductivity measurements

The molar conductances of the complexes in DMF ( $10^{-3}$  M) solutions were measured at 298 K with a Systronic model 303

direct-reading conductivity bridge at Mar Thoma College, Tiruvalla

#### Magnetic susceptibility measurements

The magnetic susceptibility measurements were performed on powdered samples at 298 K using a Sherwood Scientific Magnetic Susceptibility Balance (M.S.B) MK1 using  $\text{HgCo}(\text{SCN})_4$  as calibrant at the Department of Applied Chemistry, CUSAT, Kochi, India and the diamagnetic contribution to the susceptibility was estimated through Pascal's constants. The effective magnetic moments were calculated using the equation.

$$\mu_{\text{eff}} = 2.84(x_m T)^{1/2} \text{ BM}$$

Where T is the absolute temperature and  $X_m$  is the molar susceptibility corrected for diamagnetism of all the atoms present in the complex using pascals constants<sup>6</sup>.

#### Infrared spectroscopy

The IR spectra were recorded on a Broker Alpha II Fourier Transform Infrared spectrometer using KBr pellets in the range 4000-400  $\text{cm}^{-1}$  at the Department of Applied Chemistry, CUSAT, Kochi, India and also on a Shimadzu FT-IR Spectrophotometer with ATR technique at Mar Thoma College, Tiruvalla.

#### Electronic spectroscopy

Electronic spectra were recorded in acetonitrile solution on a Spectro UV-vis Double Beam SIMADZU 1601 spectrometer in the 200-1000 nm range.

#### EPR spectroscopy

EPR spectra of complexes were recorded in polycrystalline state at 298 K and in frozen DMF at 77 K on a Varian E-112 spectrometer at X-band, using TCNE as standard ( $g = 2.00277$ ) with 100 kHz modulation frequency and 9.1 GHz microwave frequency at SAIF, IIT Bombay, India.

**Thermogravimetric analyses**

TG-DTA-DTG analyses of the complexes were carried out under nitrogen at a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  in the range  $50\text{--}800\text{ }^{\circ}\text{C}$  using a Perkin Elmer Pyris Diamond TG/DTA analyzer at the Department of Applied Chemistry, CUSAT, Kochi, India.

**Reagents used**

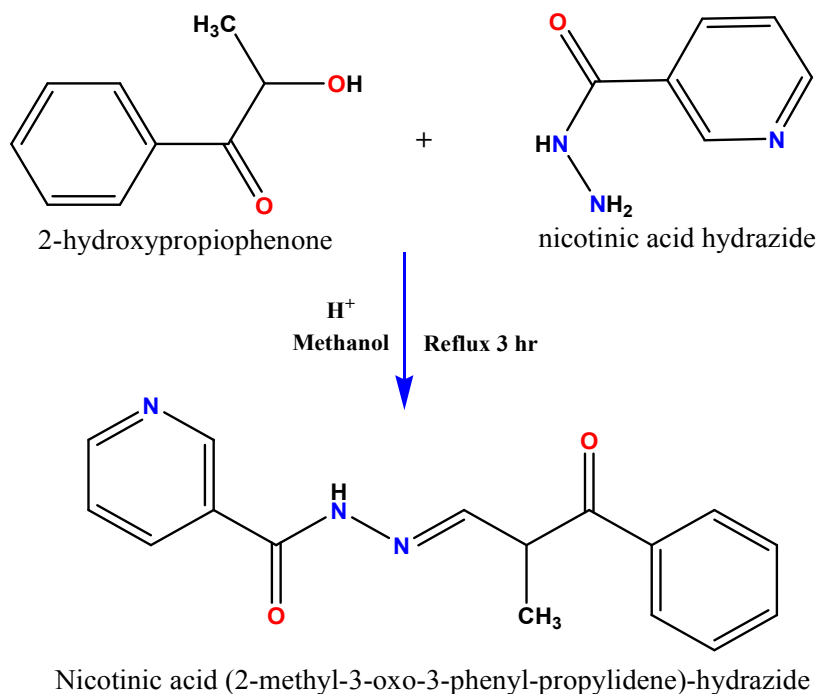
Di-2-pyridyl ketone (Aldrich), 2-benzoylpyridine (Aldrich), benzhydrazide (Aldrich), nicotinic hydrazide (Aldrich), 2-hydroxypropiophenone (Aldrich), cupric acetate (Merck), copper sulphate pentahydrate (Merck), cobalt(II) chloride dihydrate (E-Merck), nickel(II) acetate tetrahydrate (Merck), nickel(II) perchlorate hexahydrate and ammonium thiocyanate (E-Merck), were used as received.

**Syntheses of acylhydrazones**

Three ligands were synthesized by adapting the earlier reported procedure [7] and scheme for the synthesis of one of the ligand is described here

**Synthesis of 2-hydroxypropiophenone nicotinic acid hydrazone ( $\text{H}_2\text{PN}$ )**

A methanolic solution of nicotinic acid hydrazide (0.137 g, 1 mmol) was refluxed with 2-hydroxypropiophenone (0.15017 g, 1 mmol) continuously for 3 hrs after adding a drop of glacial acetic acid. There was no immediate formation of the product. Then the reaction mixture was kept aside for slow evaporation at room temperature. After 2-3 days, colourless needle shaped crystals were formed and carefully separated. The scheme for the reaction is shown below.

Scheme 1. Synthesis of  $\text{H}_2\text{L}$

### Synthesis of metal complexes of the hydrazones Synthesis of [CuLpy] (1)

To a methanolic solution of the ligand H<sub>2</sub>PN (0.269 g, 1 mmol), a base pyridine (0.409 ml, 1 mmol) is added. This is followed by the addition of methanolic solution of cupric acetate (0.199 g, 1 mmol) into it. The above green solution is refluxed continuously for 3 hrs. The green compound formed was filtered, washed with methanol and ether and dried.

### Synthesis of [CuLbipy] (2)

To a methanolic solution of the ligand H<sub>2</sub>PN (0.269 g, 1 mmol), a base 2,2'-bipyridyl (0.487 g, 1 mmol) is added. This is followed by the addition of methanolic solution of cupric acetate (0.199 g, 1 mmol) into it. The above green solution is refluxed continuously for 3 hrs. The green compound formed was filtered, washed with methanol and ether and dried.

### Synthesis of [CuLpic] (3)

To a methanolic solution of the ligand H<sub>2</sub>PN (0.269 g, 1 mmol), a base 2-picoline (0.409 g, 1 mmol) is added. This is followed by the addition of methanolic solution of cupric acetate (0.199 g, 1 mmol) into it. The above green solution is refluxed continuously for 3 hrs. The green compound formed was filtered, washed with methanol and ether and dried.

### Synthesis of [Cu<sub>2</sub>(BPB)<sub>2</sub>(μ-SO<sub>4</sub>)] (4)

To a methanolic solution of CuSO<sub>4</sub>·5H<sub>2</sub>O (0.249 g, 1 mmol), methanolic solution of the hydrazone HBPB (0.301 g, 1 mmol) was added dropwise while the mixture was stirred. The final solution was refluxed for 4 h. and on slow evaporation green crystalline

compound was separated after two days which was washed with methanol followed by ether and dried over P<sub>4</sub>O<sub>10</sub> in vacuo.

### Results and Discussions

The synthesized hydrazones and complexes have been characterized using different physic-chemical techniques described below

### Characterization of the ligands

#### Elemental analyses

C, H, N analyses of the synthesized hydrazones were consistent with that of the formulae suggested.

**HBPB:** Yield: 79%, M. P.: 129 °C. Elemental Anal. Found (Calcd.) (%): C: 75.46 (75.73), H: 5.23 (5.02), N: 13.98 (13.94).

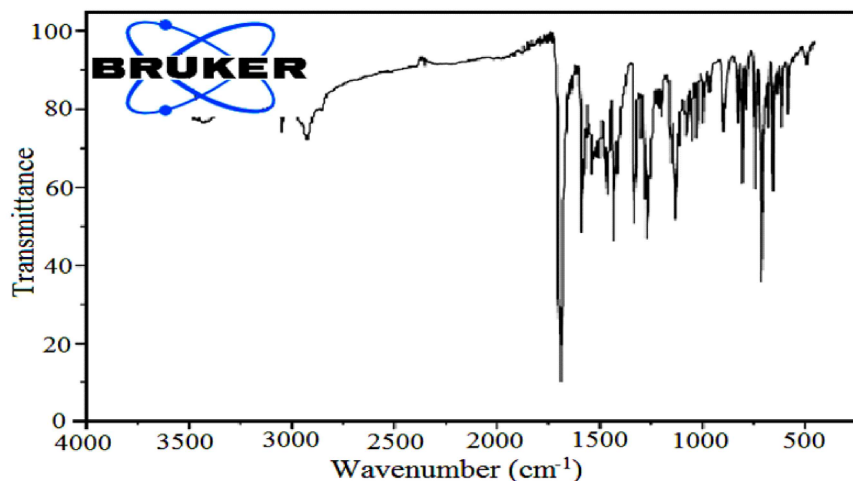
**H<sub>2</sub>PN:** Yield: 79%, Color: colorless, M.P.: 162 °C, Elemental Anal. Found (Calcd.) (%): C: 71.21(71.62), H: 5.88(6.01), N: 10.21(10.44)

### Infrared spectral studies

The IR spectra of the hydrazones have been analyzed in the region 4000-400 cm<sup>-1</sup> and the bands of diagnostic importance and their tentative assignments are listed in Table 1. Strong bands due to the δ(NH) and δ(C=O) modes at 3063 and 1678 cm<sup>-1</sup> are observed in the spectrum of HBPB (Fig. 2) which suggests that the hydrazone exists in the amido form in the solid state. A prominent band at 1571 cm<sup>-1</sup> due to azomethine ν(C=N) linkage is observed in the spectrum [8] indicating that condensation between ketone moiety of carbonyl compound and that of the hydrazide has taken place resulting into the formation of desired ligand HBPB.

**Table -1**  
**Selected infrared spectral data (cm<sup>-1</sup>) of the hydrazones**

| Compound          | ν(N-H) / ν(O-H) | ν(C=O) | ν(C=N) |
|-------------------|-----------------|--------|--------|
| HBPB              | 3063            | 1678   | 1571   |
| H <sub>2</sub> PN | 2975            | 1537   | 1643   |

Fig. 2. IR spectrum of  $H_2PN$ .**Electronic spectral studies**

The electronic spectra of the hydrazones were recorded in acetonitrile solutions ( $10^{-4}$  M) and the absorption bands are summarized in Table 3.2. The bands observed in the UV spectra of ligands corresponds to the  $n-\pi^*$  and  $\pi-\pi^*$  transitions associated with azomethine chromophore and the pyridyl rings of the hydrazones<sup>9</sup> (Fig. 3).

**Table - 2.**  
**Important bands ( $cm^{-1}$ ) of the electronic spectra of hydrazones**

| Compound | Absorption bands    |
|----------|---------------------|
| HBPB     | 42920, 36900, 31050 |
| $H_2PN$  | 41390, 35970, 32500 |

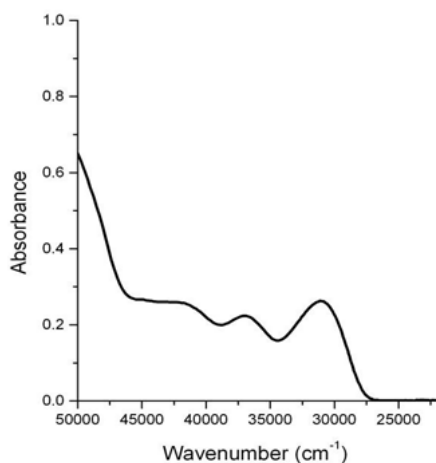
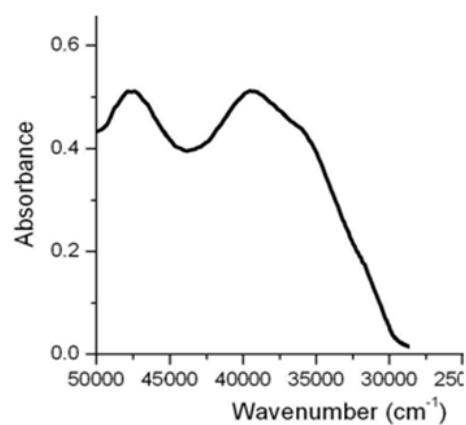
**HBPB** **$H_2PN$** 

Fig. 3. Electronic spectra of the ligands in acetonitrile solution.

### Characteriation of copper complexes of acylhydrazones

The analytical data show that the found and calculated values of the percentage of elements are in good agreement.

[CuLbipy] (**2**): Yield: 79%, Elemental Anal. Found (Calcd.) (%): 63.97(64.25), H: 4.10(4.56), N: 10.96(11.53)

[CuLpic] (**3**): Yield: 79%, Elemental Anal. Found (Calcd.) (%): C: 62.3 (62.47), H: 4.86 (5.00), N: 9.27 (9.93)

[Cu<sub>2</sub>(BPB)<sub>2</sub>(μ-SO<sub>4</sub>)] (**4**): Yield: 73%, Elemental Anal. Found (Calcd.) (%): C: 54.96 (55.40), H: 3.22 (3.43), N: 9.89 (10.20), Cu: 15.42 (15.43).

### Infrared spectra

The important infrared spectral bands of the hydrazone and complexes along with their tentative assignments are given in Table 3. Exhaustive comparisons of the selected

vibrational bands of the free hydrazone with its copper complexes give information about the ligating mode of the ligand upon complexation. The  $\nu(\text{OH})$  and  $\nu(\text{C}=\text{O})$  stretching bands at 1294 and 1650  $\text{cm}^{-1}$  respectively, corresponding to the free ligand are not observed in the spectra of the complexes. The absence of  $\nu(\text{O}-\text{H})$  and  $\nu(\text{C}=\text{O})$  bands in the metal complex, indicates that the ligand undergoes keto-enol tautomerization during complexation and the bonding occurs through an enolate O [10]. Due to the bonding of ligand with metal through a deprotonated C-O group, a new C-O band is obtained. The band assigned to the  $\nu(\text{C}=\text{N})$  stretching vibrations of the ligand is shifted to lower wavenumber on complexation with the metal, which supports the participation of azomethine group of the ligand in binding to the Cu(II) ion. Also, a new band around 1590  $\text{cm}^{-1}$  is seen suggesting the formation of new C=N bond.

**Table 3.**  
**Infrared spectral data and assignments of ligand and copper complexes.**

| S.N. | Ligand/complex                                                         | $\nu(\text{OH})$ | $\nu(\text{C}=\text{O}) / (\text{C}-\text{O})$ | $\nu(\text{C}=\text{N})$ | $\nu(\text{C}=\text{N})_{\text{new}}$ |
|------|------------------------------------------------------------------------|------------------|------------------------------------------------|--------------------------|---------------------------------------|
| 1    | H <sub>2</sub> PN                                                      | 2975             | 1537                                           | 1643                     | -                                     |
| 2    | [CuLpy] ( <b>1</b> )                                                   | -                | 1228                                           | 1540                     | 1580                                  |
| 3    | [CuLbipy] ( <b>2</b> )                                                 | -                | 1228                                           | 1532                     | 1592                                  |
| 4    | [CuLpic] ( <b>3</b> )                                                  | -                | 1294                                           | 1527                     | 1585                                  |
| 5    | HBPB                                                                   | 3063             | 1678                                           | 1571                     | -                                     |
| 6    | [Cu <sub>2</sub> (BPB) <sub>2</sub> (μ-SO <sub>4</sub> )] ( <b>4</b> ) | -                | 1370                                           | 1560                     | 1596                                  |

### Electronic Spectra

The important electronic spectral bands of the hydrazones and complexes along with their tentative assignments are given in Table 4. On complexation these bands suffer marginal shifts. The Cu(II) complexes with  $d^9$  configuration is expected to experience Jahn-Teller distortion which leads to further splitting of the  ${}^2E_g$  and  ${}^2T_{2g}$  levels and give rise to three spin allowed transitions are expected viz.  ${}^2A_{1g} \leftarrow {}^2B_{1g}$ ,  ${}^2B_{2g} \leftarrow {}^2B_{1g}$ ,  ${}^2E_g \leftarrow {}^2B_{1g}$  which occur in the ranges 11760-18180, 15500-18010 and 17240-20000  $\text{cm}^{-1}$  respectively. But often these theoretical

expectations are unseen in practice and these bands usually appear overlapped and become difficult to resolve into separate bands due to the very small energy difference between the  $d$  levels. The presence of a broad band in all the complexes in the range 14000 – 15060  $\text{cm}^{-1}$  can be assigned to the envelope of  ${}^2A_{1g} \leftarrow {}^2B_{1g}$ , range 21000-26000  $\text{cm}^{-1}$  in  ${}^2B_{2g} \leftarrow {}^2B_{1g}$ ,  ${}^2E_g \leftarrow {}^2B_{1g}$  transitions. The intense bands observed in the all Cu(II) complexes are mainly due to the phenoxy  $\text{O} \rightarrow \text{Cu(II)}$  charge transfer transitions<sup>11,12</sup>.

**Table 4.**  
**Electronic spectral data and assignments of ligand and complexes**

| Sl. No. | Compound                                                      | Absorption Bands (cm <sup>-1</sup> ) |
|---------|---------------------------------------------------------------|--------------------------------------|
| 1       | H <sub>2</sub> PN                                             | 41390, 35970, 32500                  |
| 2       | [CuLpy] (1)                                                   | 37450, 25250, 14180                  |
| 3       | [CuLbipy] (2)                                                 | 39520, 35970 (sh), 25180, 14640      |
| 4       | [CuLpic] (3)                                                  | 39520, 36630 (sh), 25770, 14300      |
| 5       | HBPB                                                          | 42920, 36900, 31050                  |
| 6       | [Cu <sub>2</sub> (BPB) <sub>2</sub> (μ-SO <sub>4</sub> )] (4) | 37950, 33980, 25430, 15030           |

### EPR spectral studies

This method is an essential tool for the analysis of the structure of molecular systems or ions containing unpaired electrons, which have spin-degenerate ground states in the absence of magnetic field. The basis of EPR lies in the spin of an electron and its associated magnetic moment. When a molecule or compound with an unpaired electron is placed in a strong magnetic field, the spin of the unpaired electron can align in two different ways creating two spin states,  $m_s = +1/2$  or  $-1/2$ . The lower energy state occurs when the magnetic moment of the electron,  $\mu$ , is aligned with the magnetic field and higher energy state occurs where  $\mu$  is aligned against the magnetic field.

For example, in case of Cu(II), the electronic configuration is [Ar] 3d<sup>9</sup>. It has one unpaired electron which is responsible for paramagnetism. When a Cu(II) compound is placed in a magnetic field, it gives a broad resonance line.

The complex **4**, in polycrystalline state at 298 K showed only one broad signal with  $g_{iso} = 2.099$ . Such isotropic spectra consisting of only one broad signal and hence only one  $g$  value ( $g_{iso}$ ), arise from extensive exchange coupling through misalignment of the local molecular axes between the different molecules in the unit cell (dipolar broadening) and enhanced spin lattice relaxation. This type of spectra unfortunately give no

information on the electronic ground state of the Cu(II) ions present in the complex. But a half field signal indicates the presence of dimeric species which arises due to the " $M_s = \pm 2$  transitions"<sup>13</sup> (Fig. 4). However in frozen DMF at 77 K, an axial spectrum was observed with four hyperfine splittings. Moreover in the perpendicular region five splittings are seen which corresponds due to the interaction of the electron with nuclear spin of two nitrogens ( $2 \times 2 \times 1 + 1 = 5$ ), which gives an evidence for the coordination of pyridyl and azomethine nitrogens. The most important aspect found in the spectrum is the presence of a half field signal with seven hyperfine splittings (Fig. 3.6) due to the coupling of the electron spin with the nuclear spin of the two Cu centers ( $2nI + 1 = 2 \times 2 \times \frac{3}{2} + 1$ ). This aspect is rarely found and is a good evidence for the dimeric species.

EPR spectra of some of the complexes are shown below

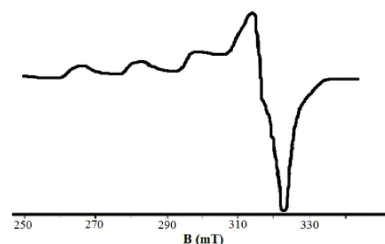


Fig. 4. EPR spectrum of [CuLpy] (1) in DMF at 77 K.

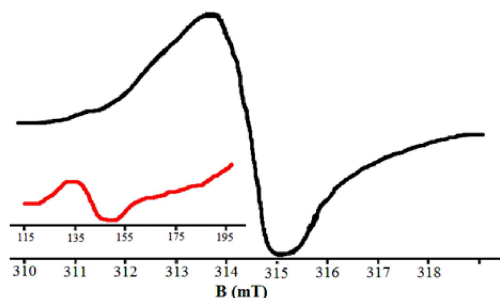


Fig. 5. EPR spectrum of  $[\text{Cu}_2(\text{BPB})_2(\mu\text{-SO}_4)]$  (4) in polycrystalline state in 298 K

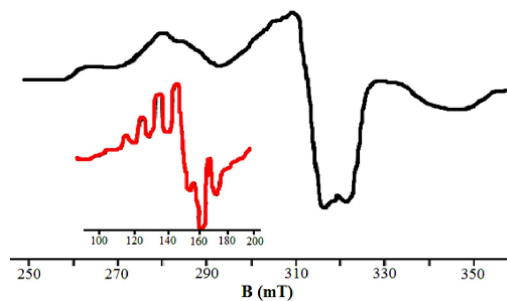


Fig. 6. EPR spectrum of  $[\text{Cu}_2(\text{BPB})_2(\mu\text{-SO}_4)]$  (4) in DMF at 77 K

## References

- 1 M.M. Heravi, L. Ranjbar, F. Derikvand, H.A. Oskooie, F.F. Bamoharram, *J. Mol. Catal. A: Chem.* **265**, 186 (2007).
- 2 R.C. Maurya, S. Rajput, *J. Mol. Struct.* **833**, 133 (2007).
- 3 U.O. Ozmen, G. Olgun, *Spectrochim. Acta Part A* **70**, 641 (2008).
- 4 N. Ozbek, G. Kavak, Y. Ozcan, S. Ide, N. Karacan, *J. Mol. Struct.* **919**, 154 (2009).
- 5 O. Pouralimardan, A.-C. Chamayou, C. Janiak, H.H. Monfared, *Inorg. Chim. Acta* **360**, 1599 (2007).
- 6 P.W. Selwood, *Magnetochemistry*, Interscience, New York (1958).
- 7 P.V. Bernhardt, G.J. Wilson, P.C. Sharpe, D.S. Kalinowski, Des R. Richardson, *J. Biol. Inorg. Chem.* **13**, 107 (2008).
- 8 M. Carcelli, P. Cozzini, T. Maccagni, C. Pelizzi, L. Righi, *Inorg. Chim. Acta* **303**, 238 (2000).
- 9 W. Kemp, *Organic Spectroscopy*, 3<sup>rd</sup> edn., Macmillan, Hampshire (1996).
- 10 R.C. Maurya, S. Rajput, *J. Mol. Struct.* **833**, 133 (2007).
- 11 M. Singh, V. Aggarwal, U.P. Singh, N.K. Singh, *Polyhedron* **28**, 195 (2009).
- 12 A.B.P. Lever, *Inorganic Electronic Spectroscopy*, 2<sup>nd</sup> edition, Elsevier, Amsterdam, 1984.
- 13 B.J. Hathaway, G. Wilkinson, R.D. Gillard, J.A. Mc Cleverty (Eds.), *Comprehensive Coordination Chemistry*, vol. 5. Pergamon, Oxford, **533** (1987).