### Accepted Manuscript

Synthesis, structure and electrochemistry behavior of a Cobalt (III) compound with azide and methyl 2-pyridyl ketone semicarbazone ligands

Behrouz Shaabani, Ali Akbar Khandar, Farzaneh Mahmoudi, Salete S. Balula, Luís Cunha-Silva

| PII:           | S0022-2860(13)00272-X                            |
|----------------|--|
| DOI:           | http://dx.doi.org/10.1016/j.molstruc.2013.03.049 |
| Reference:     | MOLSTR 19642                                     |
| To appear in:  | Journal of Molecular Structure                   |
| Received Date: | 5 November 2012                                  |
| Revised Date:  | 23 March 2013                                    |
| Accepted Date: | 25 March 2013                                    |



Please cite this article as: B. Shaabani, A.A. Khandar, F. Mahmoudi, S.S. Balula, L. Cunha-Silva, Synthesis, structure and electrochemistry behavior of a Cobalt (III) compound with azide and methyl 2-pyridyl ketone semicarbazone ligands, *Journal of Molecular Structure* (2013), doi: http://dx.doi.org/10.1016/j.molstruc.2013.03.049

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

| 1            | Synthesis, structure and electrochemistry behavior of a Cobalt (III)  |  |  |  |  |  |  |  |
|--------------|---|--|--|--|--|--|--|--|
| 2            | compound with azide and methyl 2-pyridyl ketone semicarbazone ligands   |  |  |  |  |  |  |  |
| 3            | Behrouz Shaabani <sup>1*</sup> , Ali Akbar Khandar <sup>1</sup> , Farzaneh Mahmoudi <sup>1</sup> ,  |  |  |  |  |  |  |  |
| 4            | 4 Salete S. Balula <sup>2</sup> and Luís Cunha-Silva <sup>2*</sup>  |  |  |  |  |  |  |  |
| 5            | <sup>1</sup> Department of Inorganic Chemistry, Faculty of Science, Tabriz University 51666-14766, Iran   |  |  |  |  |  |  |  |
| 6            | <sup>2</sup> REQUIMTE & Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto,   |  |  |  |  |  |  |  |
| 7            | 4169-007 Porto, Portugal  |  |  |  |  |  |  |  |
| 8<br>9<br>10 | * Corresponding authors: Behrouz Shaabani, <u>b.shaabani@yahoo.com</u> , Tel: +98 411 3393144; Fax: +98 411 3340191<br>Luís Cunha-Silva, <u>l.cunha.silva@fc.up.pt</u> , Tel: +351 220402576; Fax: +351 220402659 |  |  |  |  |  |  |  |

### 11 Abstract

An unprecedented cobalt(III) compound with methyl 2-pyridyl ketone semicarbazone (HL) and the 12 auxiliary azide ligand,  $[Co(L)_2]$   $[Co(L)(N_3)_3]$  (1) was synthesized and further characterized 13 crystallographically and spectroscopically. Compound 1 crystallizes in the triclinic system and space 14 group of P-1 and its structure consists of two mononuclear crystallographic units with metal 15 chromophore comprising two cobalt(III) centers revealing distorted octahedral geometries and 16 17 formed by distinct ligands in the inner coordination spheres. Interestingly, compound 1 represents the first complex formed by two distinct mononuclear units involving this ligand. As consequence of 18 19 various donor and acceptor groups in both crystallographic units, there are several strong N-H···N and N-H-O hydrogen bonding interactions interconnecting adjacent moieties, ultimately leading to 20 a three-dimensional supramolecular network. Furthermore, the electrochemical behavior of the HL 21 22 and compound 1 were investigated.

23 *Keywords:* Semicarbazone ligand, Azide compound, Cobalt(III) center, Crystal structure, Cyclic voltammogram.

### 24 **1. Introduction**

25 For decades, Schiff bases have been played an extraordinary role as chelating ligands in main group and transition metal coordination chemistry, due to their uncomplicated synthesis, wide availability 26 and structural versatility associated with their potential in diverse applications [1-10]. Numerous 27 Schiff bases and coordination complexes with this extensive family of ligands have revealed 28 remarkable antimicrobial activity, being potent antibacterial, antifungal, anticancer and antiviral 29 compounds[11–21]. In particular the semi and thiosemicarbazones are versatile ligands that have 30 attracted the scientific interest of researchers, not only due to their interesting coordination 31 proprieties since they can coordinate in both neutral and anionic forms [22-24], but also as 32 consequence of their potential in pharmacological applications [25–36]. Frequently, their metal 33 complexes revealed enhanced antimicrobial activities than the free Schiff base ligands. 34 35 Consequently, the design and preparation of novel coordination complexes with transition metals and semicarbazones ligands to improve and tune the proprieties trough the discovery of new structures is 36 still a notable scientific challenge. In an earlier paper [36] we have reported the synthesis of ligand 37 namely pyridine-2-carbaldehyde semicarbazone, here we report the synthesis and characterization of 38 a novel ligand methyl 2-pyridyl ketone semicarbazone (HL) (scheme 1) and the cobalt(III) 39 compound of it. The methyl 2-pyridyl ketone semicarbazone ligand has been utilized in the 40 preparation of metal complexes, A survey in the Cambridge Structural Database showed 41 demonstrated five crystal structures involving this ligand, all of them featuring mononuclear 42 43 complexes. On the other hand, a basic possibility to improve the structural features of the semicarbazones based coordination complexes is the use of auxiliary bridging ligands, such as 44 pseudohalides. These can form bridging complexes with transition metals where the groups  $N_3^-$ , 45 NCS<sup>-</sup>, NCO<sup>-</sup> coordinate in the end-to-end and end-on bridging modes [37–46]. Recently mono and 46

dinuclear complexes of Schiff base ligands and pseudohalides like azide with Cobalt(III), have been
well established [44–50].

Following our interest in the design and development of unprecedented transition metal coordination complexes with semicarbazone-type ligands and a second bridging ligand, we synthesized the Co(III) compound  $[Co(L)_2]$   $[Co(L)(N_3)_3]$  (1), with the HL and azide ligand. This compound was characterized by IR and UV spectroscopies and the solid-state structure was unveiled by single-crystal X-ray diffraction revealing two distinct mononuclear Co(III) unites,  $[Co(L)_2]$  and  $[Co(L)(N_3)_3]$ . The supramolecular interations between the different unities were investigated, and the electrochemical behavior of the free semicarbazone ligand and the compound 1 was studied.



56

57

Scheme 1. The Schiff base ligand methyl 2-pyridyl ketone semicarbazone (HL)

58

### 59 **2. Experimental**

### 60 2.1. Materials and general methods

All chemicals and solvents were of reagent grade and used as received from Merck or Fluka. Microanalyses were carried out using a Heraeus CHN–O– Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded on a FT-IR Spectrometer Bruker Tensor 27 in the region 4000–400 cm-1 using KBr pellets. UV spectra were recorded on a Shimadzu, UV-1650 PC spectrophotometer. The solid state electronic absorption spectra were recorded by diffuse reflectance spectra (DRS) on a Scinco 4100 in the range of 200-1100 nm using BaSO4 as reference. Cyclic voltammetric measurements were performed using an

AMEL Instruments Model 2053 as potentiostate connected with a function generator (AMEL Model 68 568). In all electrochemical studies, a three-electrode system was used consisting of a glassy carbon 69 as the working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl as the reference 70 71 electrode. All of the electrochemical experiments were carried out under nitrogen atmosphere at room temperature using solution of compounds with concentration about 10<sup>-3</sup> M in DMSO solvent 72 containing 0.1 M lithium perchlorate as the supporting electrolyte. Electrochemistry of HL and its 73 metal compound and azide, were studied by cyclic voltammetry in scan rate of 0.01 Vs<sup>-1</sup>. Ferrocene 74 (Fc) was used as the internal standard and all redox potentials were referenced to the Fc+/0 couple. 75

76

### 77 2.2. Synthesis of methyl 2-pyridyl ketone semicarbazone (HL)

The HL was prepared by condensation of methyl 2-pyridyl ketone with semicarbazide hydrochloride 78 [22, 23]. 0.8 g (7 mmol) of semicarbazide hydrochloride was added to a solution of 2-methyl Pyridyl 79 ketone (0.85 ml, 7 mmol) in 20 ml of methanol in a round bottom flask under continuous stirring. 80 The mixture was refluxed for 5 hours to produce a white suspension. The final reaction mixture was 81 filtered off and the filtrate was kept in room temperature for 10 hours. The resulting white 82 precipitation (m.p. 206 °C) was filtered off, washed with methanol and dried in air. Yield: 1.30 g 83 (5mmol, 80%), Anal. Calc. for C<sub>8</sub>H<sub>10</sub>N<sub>4</sub>O: C, 44.72; H, 4.66; N, 26.08. Found: C, 44.65; H, 4.46; 84 N, 26.08. Characteristic IR absorbtions (cm<sup>-1</sup>): 3431, 3279 m, v(NH<sub>2</sub>); 3192 m, v(N-H); 1578 s, 85 v(C=N); 1105 s, v(N-N); 1685 s, v(C=O). 86

87

### 88 **2.3.** Synthesis of $[Co(L)_2][Co(L)(N_3)_3]$ (1)

Crystals of **1** are obtained by slow diffusion in an H-shaped Tube already described in the literature [37, 51, 52]. By using 0.2 mmol of HL, 0.8 mmol of Co(OAC)<sub>2</sub>.4H<sub>2</sub>O and 1.5 mmol of NaN<sub>3</sub> in

ethanol, dark brown crystals of 1 were formed (decomposition at 300 °C) after seven days, which
were isolated, filtered off, washed with acetone and diethyl ether and dried in air. Yield: 0.12 g, 30%.
Anal. Calc. for C<sub>24</sub>H<sub>27</sub>Co<sub>2</sub>N<sub>21</sub>O<sub>3</sub>: C, 37.13; H, 3.48 ; N, 43.32. Found: C, 37.03; H, 3.28 ; N, 43.20.
Characteristic IR absorbtions (cm<sup>-1</sup>): 3441, 3301m, v(NH<sub>2</sub>); 1604 s, v(C=N); 1182 m, v(N-N); 591 m,
v(Co-N azomethine), 2023 s, v(N<sub>3</sub><sup>-</sup>).

96

### 97 **2.4. X-ray crystallography**

Crystalline material suitable for single-crystal X-ray diffraction analysis of the complex 98 [Co(L)<sub>2</sub>][Co(L)(N<sub>3</sub>)<sub>3</sub>] (HL is methyl 2-pyridyl ketone semicarbazone) was manually harvested and 99 100 mounted on a CryoLoop using appropriated oil [53]. Data were collected at 150(2) K on a Bruker X8 Kappa APEX II Charge-Coupled Device (CCD) area-detector diffractometer (Mo  $K_{\alpha}$  graphite-101 monochromated radiation was used,  $\lambda = 0.71073$  Å) controlled by the APEX2 software package [54], 102 and equipped with an Oxford Cryosystems Series 700 cryostream monitored remotely by the 103 Cryopad software [55]. Images were processed with SAINT+ [56], and data were corrected for 104 absorption by the multi-scan method implemented in SADABS [57]. The structure was solved by 105 106 the direct methods of SHELXS-97 [58,59] .allowing the immediate location of the Co atoms, with 107 the remaining non-hydrogen atoms being identified in the difference Fourier maps calculated from 108 successive full-matrix least-squares refinement cycles on F2 using SHELXL-97 [59, 60]. All non-109 hydrogen atoms were successfully refined with anisotropic displacement parameters, and hydrogen 110 atoms bounded to the carbon atoms wer placed in geometrical position [59-62]. 111 Hydrogen atoms of the NH<sub>2</sub> groups were markedly visible in difference Fourier maps and included in the structure with the N–H and H…H distances restrained to 0.90(2) and 1.50(2) Å, respectively, 112 and with  $U_{iso}$  fixed at  $1.5 \times U$ eq of the parent nitrogen atom. The highest peak (0.59 eÅ<sup>-3</sup>) was found 113

- at 1.09 Å from Co2 and the deepest hole (-0.69 eÅ<sup>-3</sup>) at 0.71 Å from Co2. Refinement details are
  summarized in the Table 1.
- 116
- 117

**Table 1** - Crystal data and structure refinement parameters for  $[Co(L)_2][Co(L)(N_3)_3]$  (1).

| Chemical Formula                           | C <sub>24</sub> H <sub>27</sub> Co <sub>2</sub> N <sub>21</sub> O <sub>3</sub> |
|--|--|
| Formula weight                             | 775.53   |
| Crystal description                        | Plate, brown   |
| Crystal size (mm)                          | $0.17 \times 0.09 \times 0.03$   |
| Temperature (K)                            | 150  |
| Crystal system                             | Triclinic  |
| Space group                                | P -1   |
| a (Å)                                      | 8.6140(4)  |
| b (Å)                                      | 13.2566(7)   |
| c (Å)                                      | 13.6042(7)   |
| α (°)                                      | 86.445(4)  |
| β(°)                                       | 84.286(3)  |
| γ(°)                                       | 82.026(3)  |
| Volume (Å3)                                | 1529.00(13)  |
| Z  | 2  |
| pcalculated (g cm-3)                       | 1.684  |
| μ (mm-1)                                   | 1.154  |
| θ range (°)                                | 3.66 - 25.41   |
| Final R indices [I>2σ(I)]                  | 0.0432( 4292)  |
| Final R indices (all data)                 | 0.1115(5551)   |
| Largest diff. peak and hole $(e^{A^{-3}})$ | 0.574 and -0.692   |

118

### 119 **3. Results and discussion**

- 120 **3.1. IR spectra**
- 121 The IR spectra of HL and compound 1, and the shifts of IR bands of ligand due to its coordination to
- 122 Co(III) cation are given in Table 2. For more information the FT-IR spectra curves of HL and 1 are

presented in Figures 1a and 1b. A medium band in 3192 cm<sup>-1</sup> in the free ligand HL, due to a  $v(^{2}N-H)$ 123 vibration, disappears in the spectra of 1, providing strong evidence for ligand coordination to the 124 Co(III) ion in the deprotonated enolate form [20,27,32]. The strong bands at 3431 and 3279 cm<sup>-1</sup> in 125 the spectra of HL, assigned to  $v(^{4}N-H)$ , shifts to higher energies in 1. Bands in 1578 and 1485 cm<sup>-1</sup> 126 suffer significant shifts in the spectra of 1, which can be attributed to v(C=N) and v(C=C) vibration 127 modes, and their mixing patterns are different from that in the spectra of HL. The positive shift of 128 bands corresponding to v(C=N) in the range 1578 cm<sup>-1</sup> in the HL to 1604 cm<sup>-1</sup> in 1, is consistent with 129 the coordination of the azomethine nitrogen to the Co(III) ions [21-24,35]. Medium bands at 591 130 cm<sup>-1</sup> corresponding to v(Co-N) further support azomethine nitrogen coordination [35,38,39]. The 131 enolization of HL is supported by the increase in v (N–N) by 77 cm<sup>-1</sup>. The absence of the v (C=O) 132 bands, present in HL at1685 cm<sup>-1</sup>, indicates the enolization of the amide functionality upon 133 coordination to the Co(III) center. Instead strong bands at 1645 cm<sup>-1</sup> are observed which are 134 characteristic of the coordination of HL in enolate forms [24-27]. Presence of a band at 1552 for 1, 135 is assigned to the newly formed v (N=C) after enolization [24]. The low energy pyridine ring in-136 plane and out-of-plane vibrations observed in the spectra of HL at 625 and 432 cm<sup>-1</sup> are shifted to 137 higher frequencies at 638 and 445  $\text{cm}^{-1}$  but for 1, which is a good indication of the coordination of 138 nitrogen of pyridine heterocycle to the metal center [24,27]. In 1, the well resolved peak at 2023 139  $cm^{-1}$  were obtained, which are assigned to coordinated azido group [40–50]. 140

141

Table 2. IR spectral assignment (cm<sup>-1</sup>) for HL and **1** 

| Compound | $v_{(C=N)}$ | <b>v</b> <sub>(N-N)</sub> | v <sub>(C=O)</sub> | <b>v</b> <sup>2</sup> <sub>(<b>N-H</b>)</sub> | $\mathbf{v}_{(\mathbf{N}-\mathbf{H})}^{4}$ | $\nu_{(Co-N \text{ azomethine})}$ | <b>v</b> <sub>(N3)</sub> |
|----------|-------------|---------------------------|--------------------|---|--|-----------------------------------|--------------------------|
| HL       | 1578        | 1105                      | 1685               | 3192  | 3431,3279                                  | -                                 |                          |
| 1        | 1604        | 1182                      | -                  | -   | 3441, 3301                                 | 591                               | 2023                     |

142



•

#### 168 **3.2. Electronic spectra**

Electronic spectral data of HL and 1 are presented in Table 3. The UV absorption bands of HL in 169 DMSO solvent exhibits charge transfer transitions at 260 and 320 nm attributed to intra-ligand 170  $\pi \to \pi^*$  transitions of the pyridyl ring and imine function of the semicarbazone moiety and a band at 171 365 nm attributed to  $n \rightarrow \pi^*$  transition of imine function. Metallation of HL, causes a red shift of 172 173 these electronic transitions for 1 (see Table 3). Also the absorption band at 420nm is attributed to 174 LMCT from azido ligand to cobalt(III) ions. For 1, containing distorted octahedral cobalt(III) centers, the absorption band at 600 nm appeared due to d-d transition as reported in the literature 175 176 [44,45,47] and the higher energy band was overlapped by ligand to metal charge transfer bands. As 177 seen in Table 3 and comparing the results of electronic spectra of HL and 1 in DMSO, DMF and 178 solid state, the results demonstrate that with dissolving, intense charge-transfer bands of HL and 1 appear at low wavelengths. Such a large blue shift may be attributed to the strong interaction 179 between the solvent molecules with 1. Also by comparing the electronic spectra of HL and 1 in 180 DMSO and DMF, it is concluded that by using a polar solvent the absorption bands are shifted to 181 short wavelength which is known as hypsochromic shift. 182

183

Table 3. Electronic absorption data of HL and 1

| Compound                 | $\pi \rightarrow \pi^*_{\text{pyridine}}$ | $(M^{-1}Cm^{-1})$ | $\pi \rightarrow \pi^{2}$ | *<br>imine | $\mathbf{n}  ightarrow \pi^*_{imi}$ | ne   | LMC | Г     | d-d |     |
|--------------------------|---|-------------------|---------------------------|------------|-------------------------------------|------|-----|-------|-----|-----|
| HL(DMSO)                 | 260(sh)                                   | 8000              | 320                       | 25000      | 365(sh)                             | 2000 | -   |       | -   |     |
| HL(DMF)                  | 261(sh)                                   | 7000              | 323                       | 24000      | 362(sh)                             | 2000 | -   |       | -   |     |
| HL(Solid state)          | 278(sh)                                   |                   | 351                       |            | -                                   |      | -   |       | -   |     |
| Compound 1(DMSO)         | 263(sh)                                   | 10000             | 336                       | 16000      | -                                   |      | 420 | 14000 | 600 | 250 |
| Compound 1(DMF)          | 265                                       | 8000              | 340                       | 15000      | -                                   |      | 423 | 13000 | 604 | 100 |
| Compound 1 (Solid state) | 280                                       |                   | 361                       |            | -                                   |      | 462 |       | 643 |     |

### 186 **3.3.** Crystal structure of [Co(L)<sub>2</sub>][Co(L)(N<sub>3</sub>)<sub>3</sub>](1)

The structure of 1 is depicted in Figure 2, and the crystallographic data and structure analysis for it, 187 is summarized in Table 1. The structure of 1 consists of two distinct mononuclear crystallographic 188 189 units, which will be denoted as parts A and B. In part A with formula  $[Co(L)_2]$ , the cobalt(III) center 190 is uniquely coordinated by two deprotonated HL. The structural study reveals that the Co1 center 191 exhibit a distorted octahedral environment and the equatorial sites of Co1 center are occupied by two 192 nitrogen and one enolate oxygen atoms of the HL (N5, N6 and O2) and one nitrogen atom of the second HL (N2), and the axial sites are occupied by one nitrogen and one enolate oxygen atoms of 193 194 the second HL (N1, O1). The coordination polyhedron around Co1 may be described as an axially 195 elongated octahedral (for more information about the bond length see Table 4). The Co(III)-N distances are shorter for the azomethine nitrogen atoms, indicating their stronger coordination than 196 197 pyridyl nitrogens. The angles around the Co1 center deviate significantly from 90°, the N2–Co1–O2 and N5–Co1–N2 angles have opened up to 95.16° and 98.67°, respectively and the N6–Co1–O2 and 198 N5-Co1-N6 angles have reduced to 82.68° and, 83.18° indicating distortion from a regular 199 octahedron [44,46]. The chelate bite angles in the two five-membered rings are close [O1–Co1–N2, 200 92.09°; N2-Co1-N1, 93.12° and O2-Co1-N6, 82.68°; N6-Co1-N5, 83.51°]. In part B with formula 201  $[Co(L)(N_3)_3]$ , the Co2 center is uniquely hexa coordinated by a tridentate Schiff base HL and three 202 203 terminal azides. The coordination polyhedron around Co2 is best described as distorted octahedral. 204 Distortion from the ideal octahedral geometry is mainly due to the asymmetric nature of the bond 205 tridentate Schiff base ligand. Three atoms (N9, N10 and O3) of the tridentate HL in combination 206 with three nitrogen atoms (N13, N16 and N19) of three different azides in a meridional alignment 207 complete octahedral coordination of the Co2 ion. The equatorial positions are occupied by the two nitrogen and one enolate oxygen atoms of the HL (N9, N10 and O3) and one nitrogen atom of the 208

terminal azide (N16), while other nitrogen atoms of the remaining azides (N13 and N19) are placed 209 at the axial positions with the angle of N13-Co2-N19; 178.05(12) °. The chelate bite angles in the 210 two five-membered rings are very close [O3-Co2-N10 is 82.00°, N10-Co2-N9 is 83.15°]. The 211 coordination polyhedron around Co2 may be described as an axially elongated octahedral. As seen, 212 the Co(III)-N distance is shorter for the azomethine nitrogen atom indicating its stronger 213 coordination than pyridyl and azide nitrogens. The terminal azide ligands show asymmetric N-N 214 distances of 1.198(4) /1.160(4) Å, 1.207(4) /1.167(4) and 1.208(4) /1.144(4) Å with the longer N-N 215 bonds involving the N atoms coordinated to the metal centre. The bond length for Co-N<sub>(azido)</sub> with 216 Co-N13; 1.971(3) Å, Co-N16; 1.949(3) Å, Co-N19; 1.956(5) Å are similar with that reported in the 217 literature [44-47]. The azides are quasi-linear with N–N–N angles: [N13–N14–N15; 176.7(4)°, N16– 218 N17-N18; 177.9(4) ° and N19-N20-N21; 176.6(4) °], these N-N-N angles are similar with that 219 reported in the literature [44, 47]. 220



221

222

223

224

**Figure 2.** The two neutral mononuclear crystallographic units that compose the structure of **1**, showing the labeling scheme for the Co(III) coordination centers. For clarity reasons only the hydrogen atoms of the amine groups are shown.

| Co1-N21.860(3)Co2-N101.862(3)Co1-N61.861(3)Co2-N91.917(3)Co1-O21.896(2)Co2-O31.944(3)Co1-N51.909(3)Co2-N161.949(3)Co1-N11.916(3)Co2-N191.956(3)Co1-O11.922(2)Co2-N131.971(3)N2-Co1-N6177.83(12)N10-Co2-N983.13(13)N2-Co1-O295.16(10)N10-Co2-O382.03(11)N6-Co1-O282.68(10)N9-Co2-O3165.15(11)N2-Co1-N598.67(12)N10-Co2-N16177.61(13)N6-Co1-N583.50(12)N9-Co2-N1698.81(13)O2-Co1-N5166.15(10)O3-Co2-N1696.02(12)N2-Co1-N183.15(11)N10-Co2-N1988.59(12)O2-Co1-N197.04(11)N9-Co2-N1990.36(12)N5-Co1-N190.98(11)N16-Co2-N1390.65(12)N2-Co1-O182.09(10)N10-Co2-N1390.92(12)O2-Co1-O192.39(10)O3-Co2-N1389.64(11)N5-Co1-O190.38(11)N16-Co2-N1390.72(12)N1-Co1-O1165.21(10)N19-Co2-N13178.06(12) |
|--|
| Co1-N61.861(3)Co2-N91.917(3)Co1-O21.896(2)Co2-O31.944(3)Co1-N51.909(3)Co2-N161.949(3)Co1-N11.916(3)Co2-N191.956(3)Co1-O11.922(2)Co2-N131.971(3)N2-Co1-N6177.83(12)N10-Co2-N983.13(13)N2-Co1-O295.16(10)N10-Co2-O382.03(11)N6-Co1-O282.68(10)N9-Co2-O3165.15(11)N2-Co1-N598.67(12)N10-Co2-N16177.61(13)N6-Co1-N583.50(12)N9-Co2-N1698.81(13)O2-Co1-N183.15(11)N10-Co2-N1987.44(12)N6-Co1-N197.04(11)N9-Co2-N1988.59(12)O2-Co1-N189.80(11)O3-Co2-N1990.36(12)N5-Co1-O190.98(11)N10-Co2-N1390.65(12)N6-Co1-O197.74(10)N9-Co2-N1389.64(11)N5-Co1-O190.38(11)N16-Co2-N1389.64(11)N5-Co1-O190.38(11)N16-Co2-N13178.06(12)  |
| Co1-O21.896(2)Co2-O31.944(3)Co1-N51.909(3)Co2-N161.949(3)Co1-N11.916(3)Co2-N191.956(3)Co1-O11.922(2)Co2-N131.971(3)N2-Co1-N6177.83(12)N10-Co2-N983.13(13)N2-Co1-O295.16(10)N10-Co2-O382.03(11)N6-Co1-O282.68(10)N9-Co2-O3165.15(11)N2-Co1-N598.67(12)N10-Co2-N1697.61(13)N6-Co1-N583.50(12)N9-Co2-N1696.02(12)N2-Co1-N183.15(11)N10-Co2-N1988.1(13)O2-Co1-N183.15(11)N10-Co2-N1988.59(12)N2-Co1-N189.80(11)O3-Co2-N1696.02(12)N2-Co1-N189.80(11)N16-Co2-N1980.612)N2-Co1-N190.98(11)N16-Co2-N1390.92(12)N2-Co1-O192.39(10)O3-Co2-N1389.64(11)N5-Co1-O190.38(11)N16-Co2-N1390.72(12)N1-Co1-O1165.21(10)N19-Co2-N13178.06(12)  |
| Co1-N51.909(3)Co2-N161.949(3)Co1-N11.916(3)Co2-N191.956(3)Co1-O11.922(2)Co2-N131.971(3)N2-Co1-N6177.83(12)N10-Co2-N983.13(13)N2-Co1-O295.16(10)N10-Co2-O382.03(11)N6-Co1-O282.68(10)N9-Co2-O3165.15(11)N2-Co1-N598.67(12)N10-Co2-N16177.61(13)N6-Co1-N583.50(12)N9-Co2-N1698.81(13)O2-Co1-N5166.15(10)O3-Co2-N1696.02(12)N2-Co1-N183.15(11)N10-Co2-N1987.44(12)N2-Co1-N189.80(11)O3-Co2-N1990.36(12)N5-Co1-N190.98(11)N16-Co2-N1390.65(12)N2-Co1-O182.09(10)N10-Co2-N1390.92(12)O2-Co1-O192.39(10)O3-Co2-N1389.64(11)N5-Co1-O190.38(11)N16-Co2-N1390.72(12)N1-Co1-O1165.21(10)N19-Co2-N13178.06(12)  |
| Co1-N11.916(3)Co2-N191.956(3)Co1-O11.922(2)Co2-N131.971(3)N2-Co1-N6177.83(12)N10-Co2-N983.13(13)N2-Co1-O295.16(10)N10-Co2-O382.03(11)N6-Co1-O282.68(10)N9-Co2-O3165.15(11)N2-Co1-N598.67(12)N10-Co2-N16177.61(13)N6-Co1-N583.50(12)N9-Co2-N1698.81(13)O2-Co1-N5166.15(10)O3-Co2-N1696.02(12)N2-Co1-N183.15(11)N10-Co2-N1987.44(12)N6-Co1-N197.04(11)N9-Co2-N1988.59(12)O2-Co1-N189.80(11)O3-Co2-N1990.36(12)N5-Co1-N190.98(11)N16-Co2-N1991.21(13)N2-Co1-O182.09(10)N10-Co2-N1390.92(12)O2-Co1-O197.74(10)N9-Co2-N1389.64(11)N5-Co1-O190.38(11)N16-Co2-N1390.72(12)N1-Co1-O1165.21(10)N19-Co2-N13178.06(12)  |
| Co1-O11.922(2)Co2-N131.971(3)N2-Co1-N6177.83(12)N10-Co2-N983.13(13)N2-Co1-O295.16(10)N10-Co2-O382.03(11)N6-Co1-O282.68(10)N9-Co2-O3165.15(11)N2-Co1-N598.67(12)N10-Co2-N16177.61(13)N6-Co1-N583.50(12)N9-Co2-N1698.81(13)O2-Co1-N5166.15(10)O3-Co2-N1696.02(12)N2-Co1-N183.15(11)N10-Co2-N1987.44(12)N6-Co1-N197.04(11)N9-Co2-N1988.59(12)O2-Co1-N189.80(11)O3-Co2-N1990.36(12)N5-Co1-O190.98(11)N10-Co2-N1390.65(12)N6-Co1-O197.74(10)N9-Co2-N1390.92(12)O2-Co1-O192.39(10)O3-Co2-N1390.72(12)N1-Co1-O1165.21(10)N19-Co2-N13178.06(12)  |
| N2-Co1-N6177.83(12)N10-Co2-N983.13(13)N2-Co1-O295.16(10)N10-Co2-O382.03(11)N6-Co1-O282.68(10)N9-Co2-O3165.15(11)N2-Co1-N598.67(12)N10-Co2-N16177.61(13)N6-Co1-N583.50(12)N9-Co2-N1698.81(13)O2-Co1-N5166.15(10)O3-Co2-N1696.02(12)N2-Co1-N183.15(11)N10-Co2-N1987.44(12)N6-Co1-N197.04(11)N9-Co2-N1988.59(12)O2-Co1-N189.80(11)O3-Co2-N1990.36(12)N5-Co1-N190.98(11)N16-Co2-N1390.65(12)N6-Co1-O197.74(10)N9-Co2-N1390.92(12)O2-Co1-O192.39(10)O3-Co2-N1389.64(11)N5-Co1-O190.38(11)N16-Co2-N1390.72(12)N1-Co1-O1165.21(10)N19-Co2-N13178.06(12)   |
| N2-Co1-O295.16(10)N10-Co2-O382.03(11)N6-Co1-O282.68(10)N9-Co2-O3165.15(11)N2-Co1-N598.67(12)N10-Co2-N16177.61(13)N6-Co1-N583.50(12)N9-Co2-N1698.81(13)O2-Co1-N5166.15(10)O3-Co2-N1696.02(12)N2-Co1-N183.15(11)N10-Co2-N1987.44(12)N6-Co1-N197.04(11)N9-Co2-N1988.59(12)O2-Co1-N189.80(11)O3-Co2-N1990.36(12)N5-Co1-N190.98(11)N16-Co2-N1991.21(13)N2-Co1-O182.09(10)N10-Co2-N1390.65(12)N6-Co1-O197.74(10)N9-Co2-N1390.92(12)O2-Co1-O190.38(11)N16-Co2-N1390.72(12)N5-Co1-O190.38(11)N16-Co2-N1390.72(12)N1-Co1-O1165.21(10)N19-Co2-N13178.06(12)  |
| N6-Co1-O282.68(10)N9-Co2-O3165.15(11)N2-Co1-N598.67(12)N10-Co2-N16177.61(13)N6-Co1-N583.50(12)N9-Co2-N1698.81(13)O2-Co1-N5166.15(10)O3-Co2-N1696.02(12)N2-Co1-N183.15(11)N10-Co2-N1987.44(12)N6-Co1-N197.04(11)N9-Co2-N1988.59(12)O2-Co1-N189.80(11)O3-Co2-N1990.36(12)N5-Co1-N190.98(11)N16-Co2-N1991.21(13)N2-Co1-O182.09(10)N10-Co2-N1390.65(12)N6-Co1-O197.74(10)N9-Co2-N1390.92(12)O2-Co1-O192.39(10)O3-Co2-N1389.64(11)N5-Co1-O190.38(11)N16-Co2-N1390.72(12)N1-Co1-O1165.21(10)N19-Co2-N13178.06(12)  |
| N2-Co1-N598.67(12)N10-Co2-N16177.61(13)N6-Co1-N583.50(12)N9-Co2-N1698.81(13)O2-Co1-N5166.15(10)O3-Co2-N1696.02(12)N2-Co1-N183.15(11)N10-Co2-N1987.44(12)N6-Co1-N197.04(11)N9-Co2-N1988.59(12)O2-Co1-N189.80(11)O3-Co2-N1990.36(12)N5-Co1-N190.98(11)N16-Co2-N1991.21(13)N2-Co1-O182.09(10)N10-Co2-N1390.65(12)N6-Co1-O197.74(10)N9-Co2-N1390.92(12)O2-Co1-O192.39(10)O3-Co2-N1389.64(11)N5-Co1-O190.38(11)N16-Co2-N1390.72(12)N1-Co1-O1165.21(10)N19-Co2-N13178.06(12)   |
| N6-Co1-N583.50(12)N9-Co2-N1698.81(13)O2-Co1-N5166.15(10)O3-Co2-N1696.02(12)N2-Co1-N183.15(11)N10-Co2-N1987.44(12)N6-Co1-N197.04(11)N9-Co2-N1988.59(12)O2-Co1-N189.80(11)O3-Co2-N1990.36(12)N5-Co1-N190.98(11)N16-Co2-N1991.21(13)N2-Co1-O182.09(10)N10-Co2-N1390.65(12)N6-Co1-O197.74(10)N9-Co2-N1390.92(12)O2-Co1-O192.39(10)O3-Co2-N1389.64(11)N5-Co1-O190.38(11)N16-Co2-N1390.72(12)N1-Co1-O1165.21(10)N19-Co2-N13178.06(12)  |
| O2-Co1-N5166.15(10)O3-Co2-N1696.02(12)N2-Co1-N183.15(11)N10-Co2-N1987.44(12)N6-Co1-N197.04(11)N9-Co2-N1988.59(12)O2-Co1-N189.80(11)O3-Co2-N1990.36(12)N5-Co1-N190.98(11)N16-Co2-N1991.21(13)N2-Co1-O182.09(10)N10-Co2-N1390.65(12)N6-Co1-O197.74(10)N9-Co2-N1390.92(12)O2-Co1-O192.39(10)O3-Co2-N1389.64(11)N5-Co1-O190.38(11)N16-Co2-N1390.72(12)N1-Co1-O1165.21(10)N19-Co2-N13178.06(12)   |
| N2-Co1-N183.15(11)N10-Co2-N1987.44(12)N6-Co1-N197.04(11)N9-Co2-N1988.59(12)O2-Co1-N189.80(11)O3-Co2-N1990.36(12)N5-Co1-N190.98(11)N16-Co2-N1991.21(13)N2-Co1-O182.09(10)N10-Co2-N1390.65(12)N6-Co1-O197.74(10)N9-Co2-N1390.92(12)O2-Co1-O192.39(10)O3-Co2-N1389.64(11)N5-Co1-O190.38(11)N16-Co2-N1390.72(12)N1-Co1-O1165.21(10)N19-Co2-N13178.06(12)   |
| N6-Co1-N197.04(11)N9-Co2-N1988.59(12)O2-Co1-N189.80(11)O3-Co2-N1990.36(12)N5-Co1-N190.98(11)N16-Co2-N1991.21(13)N2-Co1-O182.09(10)N10-Co2-N1390.65(12)N6-Co1-O197.74(10)N9-Co2-N1390.92(12)O2-Co1-O192.39(10)O3-Co2-N1389.64(11)N5-Co1-O190.38(11)N16-Co2-N1390.72(12)N1-Co1-O1165.21(10)N19-Co2-N13178.06(12)   |
| O2-Co1-N189.80(11)O3-Co2-N1990.36(12)N5-Co1-N190.98(11)N16-Co2-N1991.21(13)N2-Co1-O182.09(10)N10-Co2-N1390.65(12)N6-Co1-O197.74(10)N9-Co2-N1390.92(12)O2-Co1-O192.39(10)O3-Co2-N1389.64(11)N5-Co1-O190.38(11)N16-Co2-N1390.72(12)N1-Co1-O1165.21(10)N19-Co2-N13178.06(12)  |
| N5-Co1-N190.98(11)N16-Co2-N1991.21(13)N2-Co1-O182.09(10)N10-Co2-N1390.65(12)N6-Co1-O197.74(10)N9-Co2-N1390.92(12)O2-Co1-O192.39(10)O3-Co2-N1389.64(11)N5-Co1-O190.38(11)N16-Co2-N1390.72(12)N1-Co1-O1165.21(10)N19-Co2-N13178.06(12)   |
| N2-Co1-O182.09(10)N10-Co2-N1390.65(12)N6-Co1-O197.74(10)N9-Co2-N1390.92(12)O2-Co1-O192.39(10)O3-Co2-N1389.64(11)N5-Co1-O190.38(11)N16-Co2-N1390.72(12)N1-Co1-O1165.21(10)N19-Co2-N13178.06(12)   |
| N6-Co1-O197.74(10)N9-Co2-N1390.92(12)O2-Co1-O192.39(10)O3-Co2-N1389.64(11)N5-Co1-O190.38(11)N16-Co2-N1390.72(12)N1-Co1-O1165.21(10)N19-Co2-N13178.06(12)   |
| O2-Co1-O192.39(10)O3-Co2-N1389.64(11)N5-Co1-O190.38(11)N16-Co2-N1390.72(12)N1-Co1-O1165.21(10)N19-Co2-N13178.06(12)  |
| N5-Co1-O190.38(11)N16-Co2-N1390.72(12)N1-Co1-O1165.21(10)N19-Co2-N13178.06(12)   |
| N1-Co1-O1 165.21(10) N19-Co2-N13 178.06(12)  |
|  |

Table 4 - Selected bond lengths (Å) and angles (deg) for 1.

As consequence of various donor and acceptor groups in both the parts, there are several strong N–H···N and N–H···O hydrogen bonds interconnecting adjacent moieties. The details about the hydrogen bonds interconnecting are summarized in Table 5. While N4–H4B···O1<sup>ii</sup> and N8–H8B···N3<sup>iii</sup> interconnect only crystallographic equivalent parts of type **A**, the remaining hydrogen bonds (N4–H4A···N11<sup>i</sup>, N8–H8A···N13 and N12–H12B···N7<sup>iv</sup>) are interaction involving distinct parts, i.e. between parts **A** and **B**. These strong hydrogen bonding network lead to the

234 formation of a three-dimensional supramolecular network. These hydrogen interactions and a three-

dimensional supramolecular network for the compound are shown in the Figures. 3a and 3b.



236

Figure 3. (a) N-H···N and N-H···O hydrogen bonds interconnecting adjacent parts A and B. (b) Extended crystalline packing showing the 3D hydrogen bonding network. Hydrogen bonds are represented as dashed lines (golden color) and for clarity only the H-atoms involved in the hydrogen bonds are shown.

- 241
- 242

 Table 5. Selected hydrogen bonding parameters for 1.

| D–Н···А                   | d(D-H)(Å) | d(H…A)(Å) | $d(D \cdots A)(A)$ | $(D-H\cdots A)(^{\circ})$ |  |
|---------------------------|-----------|-----------|--------------------|---------------------------|--|
| N4–H4A…N11 <sup>i</sup>   | 0.886(17) | 2.09(2)   | 2.943(4)           | 161(3)                    |  |
| N4-H4B…O1 <sup>ii</sup>   | 0.874(17) | 2.028(19) | 2.898(3)           | 174(3)                    |  |
| N8-H8A…N13                | 0.869(17) | 2.12(2)   | 2.969(4)           | 164(3)                    |  |
| N8-H8B…N3 <sup>iii</sup>  | 0.868(17) | 2.12(2)   | 2.963(4)           | 165(3)                    |  |
| N12–H12B…N7 <sup>iv</sup> | 0.880(18) | 2.55(3)   | 3.322(4)           | 147(4)                    |  |

Symmetry transformations used to generate equivalent atoms: (i) x-1,y,z ;

(ii) -x,-y+1,-z+1; (iii) x+1,y,z; (iv) -x+1,-y+1,-z+1

- 243
- 244
- 245
- 246

#### 247 **3.3. Electrochemistry**

#### 248 *3.3.1. Electrochemistry of the HL and azide ligands*

It is evident from the cyclic voltammogram of HL displayed in Figure 4a, that HL is electroactive over a range from 1.5 to -2.0 V in dimethylsulfoxide solvent. Two ligand-centered redox waves observed at -1.15 and 1.18 V are attributed to the pyridine rings. The azo group (-N=N-) is known as a potential electron transfer center [44] and the cyclic voltammogram of azide ligand displays only one irreversible oxidation wave at 0.85 V (see Figure 4b).

### 254 3.3.2. Electrochemistry of $[Co(L)_2][Co(L)(N_3)_3](1)$

255 As seen in Figure 5, the compound 1 exhibits both metal and ligand centred electroactivity in the 256 potential range -2 to 1V. The cyclic voltammogram of 1 in DMSO, displays two cathodic potentials 257 at about -0.54V (I<sub>c1</sub>) and -1.68V(I<sub>c2</sub>). The cathodic peaks of 1 at -0.54 (I<sub>c1</sub>) and -1.68 (I<sub>c2</sub>) (versus Ag/AgCl) can be attributed for the reduction of two cobalt(III) ions in different environment 258 to cobalt(II). During the reverse scan oxidation waves ( $I_{a1}$ ,  $I_{a2}$  and  $I_{a3}$ ) appear at -1.68, -0.54 and 259 0.94 V. The oxidation waves  $(I_{a1}, I_{a2})$  which are associated with the cathodic peaks  $I_{c2}$  and  $I_{c1}$ , 260 respectively. These processes are completely reversible, characterized by a peak to peak separation 261  $(\Delta E_p = E_{Pa} - E_{pc})$  of 0.18 and 0.16 V, respectively, which remains unchanged upon changing the scan 262 rate. There is also an equality in the anodic peak current and the cathodic peak current of 1  $(i_{a1}/i_{c2})$ 263 =0.35,  $i_{a2}/i_{c1}$  = -.080 ), as expected for an reversible electron transfer process. The oxidation waves 264  $(I_{a3})$  displays at 0.94 V is attributed to the oxidation of azide ligand [29,33]. 265

266

267

268



280 4. Conclusion

A cobalt(III) compound  $[Co(L)_2]$   $[Co(L)(N_3)_3]$  (1), involving Schiff base methyl 2-pyridyl ketone semicarbazone (HL) and the auxiliary azide ligand, has been synthesized and characterized. Comparison of the IR spectra of HL and 1, indicates that HL acts as a tridentate Schiff base and is chelated to the cobalt(III) centers in enolate form, which is confirmed by the solid-state structure

determinate by single crystal X-ray diffraction. In fact, compound 1 consists of two Co(III) 285 mononuclear crystallographic units with different coordination spheres, but both the Co(III) centers 286 are six coordinated with distorted octahedral geometries. This compound is the first compound 287 formed by two mononuclear units based in the methyl 2-pyridyl ketone semicarbazone ligand. As 288 consequence of various donor and acceptor groups in the two distinct units, there are several strong 289 N-H. N and N-H. O hydrogen bonds interconnecting adjacent moieties, ultimately leading to a 290 291 three-dimensional supramolecular network. Cyclic voltammetric experiments of 1 in DMSO reveals oxidation of azide at 0.94 V and two oxidation potentials at -1.68, -0.54 V for two different 292 cobalt(III) centers. Currently, we are investigating other bridging auxiliary ligands to be used with 293 294 semicarbazone based molecules in the preparation of new metal coordination compounds, in order to increase their structural complexity and improve their properties. 295

296

#### 297 Acknowledgements

We are grateful to Tabriz University of Research council for the financial support of this research. We are grateful to the
Fundação para a Ciência e a Tecnologia, (FCT, MEC, Portugal) for their general financial support under the strategic
project PEst-C/EQB/LA0006/2011.

301

#### 302 Appendix A. Supplementary data

303 Crystallographic data (excluding structure factors) for all the structures reported in this paper have been deposited with
304 the Cambridge Crystallographic Data Centre as supplementary publication no.CCDC- 894063. Copies of these data can
305 be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 2EZ, UK; FAX: (+44) 1223
306 336033, or online via www.ccdc.cam.ac.uk/data\_request/cif or by emailing data\_request@ccdc.cam.ac.uk.

307

#### 308 References

- 309 [1] S. Meghdadi, M.Amirnasr, K.Mereiter, H.Molaee, A. Amiri, Polyhedron 30 (2011) 1651–1656.
- 310 [2]G. G. Mohamed, M.A. Zayed, S.M. Abdallah, Journal of Molecular Structure 979 (2010) 62–71.

- 311 [3] C. Maxim, T. D. Pasatoiu, V. Ch. Kravtsov, S. Shova, Ch. A. Muryn, R. E.P. Winpenny, F.Tuna, M. Andruh,
- **312** Inorganica Chimica Acta 361 (2008) 3903–3911.
- 313 [4] S.Nayak, P. Gamez, B. Kozlevc'ar, A.Pevec, O. Roubeau, S. Dehnen, J. Reedijk, Polyhedron 29 (2010) 2291–2296 .
- 314 [5] G. G. Mohamed, M.M. Omar, Amr A. Ibrahim, Spectrochimica Acta Part A 75 (2010) 678–685.
- 315 [6]S. Baluja, A. Solanki, N. Kachhadia, Journal of the Iranian Chemical Society, 3 (2006) 312-317.
- 316 [7] T. Rosu , E. I. Pahontu, C. Maxim, R. Georgescu, N. Stanica, G.L. Almajan, A.Gulea, Polyhedron 29 (2010) 757-
- **317** 766.
- 318 [8] B.H. Chen, H.H. Yao, W.T. Huang, P. Chattopadhyay, J.M. Lo, T.H. Lu, Solid State Sciences t. 1 (1999) 119-131.
- 319 [9]C. Maxim, T. D. Pasatoiu, V. Ch. Kravtsov, S. Shova, Ch. A. Muryn, R. E.P. Winpenny, F. Tuna, Marius Andruh,
- **320** Inorganica Chimica Acta 361 (2008) 3903–3911.
- 321 [10] V. M. Leovac, L.S. Jovanovic', V. Divjakovic', A. Pevec, I. Leban, Th. Armbruster, Polyhedron 26 (2007) 49–58.
- 322 [11] G. G. Mohamed, M.A. Zayed, S.M. Abdallah, Journal of Molecular Structure 979 (2010) 62–71.
- 323 [12] P.F. Rapheal, E. Manoj, M.R. Prathapachandra Kurup, E. Suresh, Polyhedron 26 (2007) 607–616.
- 324 [13] S.Arulmurugan1, H.P. Kavitha1, B.R. Venkatraman, Rasayan J.chem, 3 (2010), 385-410.
- 325 [14] P.F. Rapheal, E. Manoj, M.R. Prathapachandra Kurup, Polyhedron 26 (2007) 5088–5094.
- 326 [15] U.L. Kala, S. Suma, M.R. Prathapachandra Kurup, Suja Krishnan b, Rohith P. John, Polyhedron 26 (2007) 1427–
  327 1435.
- 328 [16] D. Gambino, M. Fernández, D. Santos, G. A. Etcheverría, O. E. Piro, F. R. Pavan, C. Q.F. Leite, I. Tomaz, F.
- 329 Marques, Polyhedron 30 (2011) 1360–1366.
- [17] C. M. Silva, D. L. daSilva, L. V.Modolo, R. B. Alves, M. A.deResende, C. V.B. Martins, Â. Fátima, Journal of
  Advanced Research(2010).
- 332 [18] H. Khanmohammadi, S. Amani, M. H. Abnosi, H. R. Khavasi, Spectrochimica Acta Part A 77 (2010) 342–347.
- 333 [19] N. Raman, S. Sobha, A. Thamaraichelvan, Spectrochimica Acta Part A 78 (2011) 888–898.
- 334 [20] J. G. Tojala, J. L. Pizarro, A. Garc´ıa-Orad, A. R.P. Sanz, M. Ugalded, A.A. D´ıaze, J. L. Serra, M. I. Arriortua, T.
- **335** Rojod, Journal of Inorganic Biochemistry 86 (2001) 627–633.
- 336 [21] S. Basak, S. Sen, S. Banerjee, S. Mitra ,G. Rosair, M.T. G. Rodriguez, Polyhedron 26 (2007) 5104–5112.
- [22] N. Ch. Kasuga, K. Sekino, Ch. Koumo, N. Shimada, M. Ishikawa, K. Nomiya, Journal of Inorganic Biochemistry 84
   (2001) 55–65.
- 339 [23] N. Ch. Kasuga, K. Onodera, S. Nakano, K. Hayashi, K. Nomiya, Journal of Inorganic Biochemistry 100 (2006)
  340 1176–1186.
- 341 [24] T.A. Reena, E.B. Seena, M.R. Prathapachandra Kurup, Polyhedron 27 (2008) 1825–1831
- 342 [25] E. R. Garbelini, M. Hörner, M. B. Behm, D. J. Evans, and F.S. Nunes, Z. Anorg, Allg. Chem. (2008) 1801-1806.
- 343 [26] S. Chandr, S. Raizad, R. Verm, Journal of Chemical and Pharmaceutical Research, 4(3) (2012)1612-1618.

- 344 [27] A. Ray, S. Banerjee, Ray. J. Butcher, C. Desplanches, S. Mitra, Polyhedron 27 (2008) 2409–2415.
- 345 [28] P. Gómez-Saiz, R. Gil-García, M. A. Maestro, J. L. Pizarro, M. I. Arriortua, L. Lezama, T. Rojo, M. González-
- Alvarez, J. Borrás, J. García-Tojal, Journal of Inorganic Biochemistry 102 (2008) 1910–1920.
- 347 [29] M. C. Rodríguez-Argüelles, S. Mosquera-Vázquez, J. Sanmartín-Matalobos, A. M. García-Deibe, C. Pelizzi, F.
- 348 Zani, Polyhedron 29 (2010) 864–870.
- 349 [30] S.Chandra, A. Kumar, Spectrochimica Acta Part A 66 (2007) 1347–1351.
- 350 [31]D. Kovala-Demertzi, P. N. Yadav, J. Wiecek, S. Skoulika, T. Varadinova, M.A. Demertzis, Journal of Inorganic
- **351** Biochemistry 100 (2006) 1558–1567.
- 352 [32] P.F. Rapheal, E. Manoj, M.R. Prathapachandra Kurup, Polyhedron 26 (2007) 5088–5094.
- 353 [33] U.L. Kala, S. Suma, M.R. Prathapachandra Kurup, S. Krishnan, R. P. John, Polyhedron 26 (2007) 1427–1435.
- 354 [34] J. Garc´ıa-Tojal, J. L. Pizarro, A.Garc´ıa-Orad, A. R. Pe´rez-Sanz, M. Ugalded, A. A. D´ıaze, J. L. Serra, M. I.
- 355 Arriortua, T. Rojod, Journal of Inorganic Biochemistry 86 (2001) 627–633.
- 356 [35] P. F. Rapheal, E. Manoj, M.R. Prathapachandra Kurup, E. Suresh, Polyhedron 26 (2007) 607–616.
- 357 [36] B. Shaabani, A.A. Khandar, M. Dusek, M. Pojarova, F.Mahmoudi, Inorganica Chimica Acta 394 (2013) 563-568.
- 358 [37] W-W. Sun, X-B. Qian, Ch-Y. Tian, E-Q. Gao, Inorganica Chimica Acta 362 (2009) 2744–2748.
- 359 [38] U. Ray, B. Chand, G. Mostafa, J. Cheng, T-H. Lu, Ch. Sinh, Polyhedron 22 (2003) 2587-2594.
- 360 [39] A. Sreekanth, U.L. Kala, Chandini R. Nayar, M.R. Prathapachandra Kurup, Polyhedron 23 (2004) 41–47.
- 361
- 362 [40] Sh. Shit, P. Talukder, J. Chakraborty, G. Pilet, M. S. El Fallah, J. Ribas, S. Mitra, Polyhedron 26 (2007) 1357–1363
  363
- 364 [41] M. A.S. Goher, A. A. Youssef, F. A. Mautner, Polyhedron 25 (2006) 1531–1536
- 365 [42] Sk. H. Rahaman, H. Chowdhury, H. L. Milton, A. M.Z. Slawin, J. D. Woollins, B. K. Ghosh, Inorganic Chemistry
- **366** Communications 8 (2005) 1031–1035.
- 367 [43] X-T. Liu, Q-L. Liu. J. Mol. Struct., 889, 160 (2008).
- 368 [44] S. S. Massoud, F. A. Mautner, M. Abu-Youssef, N. M. Shuaib, Polyhedron 18 (1999) 2287–2291.
- 369 [45] F. A. Mautner, B. Sodin, R.Vicente, Inorganica Chimica Acta (2011).
- 370 [46] S. Sasi, M.R. Prathapachandra Kurup, E. Suresh, Journal of Chemical Crystallography, 37 (2007) 31-36.
- 371 [47] M. A.S. Goher, A. A. Youssef, F. A. Mautner, Polyhedron 25 (2006) 1531–1536.
- 372 [48] Sk. H.Rahaman, H.Chowdhury, H. L. Milton, A.M.Z. Slawin, J. D. Woollins, B. K. Ghosh, Inorganic Chemistry
- **373** Communications 8 (2005) 1031–1035.
- 374 [49] S. S. Massouda, F. A. Mautner, M. Abu-Youssef, N. M. Shuaibc, Polyhedron 18 (1999) 2287–2291.
- 375 [50] F. A. Mautner, B. Sodin, R. Vicente, Inorganica Chimica Acta (2011).
- 376 [51] A.A. Soudi, A.H. White, Aust. J. Chem. 49 (1996) 1029–1042.

- 377 [52] F. Marandi, B. Mirtamizdoust, A. A. Soudi, H-K. Fun, Inorganic Chemistry Communications 10 (2007) 174–177.
- **378** [53] T. Kottke and D. Stalke, J. App. Cryst., 1993, 26, 615-619.
- 379 [54] APEX2, Data Collection Software Version 2.1-RC13, Bruker AXS, Delft, The Netherlands, 2006.
- 380 [55] Cryopad, Remote monitoring and control, Version 1.451, Oxford Cryosystems, Oxford, United Kingdom, 2006.
- 381 [56] SAINT, Data Integration Engine v. 7.23a ©, 1997-2005, Bruker AXS, Madison, Wisconsin, USA.
- 382 [57] G. M. Sheldrick, SADABS v.2.01, Bruker/Siemens Area Detector Absorption Correction Program, 1998, Bruker

MAT

- 383 AXS, Madison, Wisconsin, USA.
- 384 [58] G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, 1997.
- 385 [59] G. M. Sheldrick, Acta Cryst. A, 2008, 64, 112-122.
- 386 [60] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, 1997.
- 387 [61] A. Thorn, B. Dittrich and G. M. Sheldrick, Acta Cryst. (2012). A68, 448-451
- 388 [62] G. M. Sheldrick, Acta Cryst. (2010). D66, 176-180

- Dear Reviewer 390
- 391 We acknowledge the reviewer helpful and relevant comments. We revised the manuscript according
- 392 to your comments. we submit the revised manuscript that are highlighted in green for response to
- 393 your comments.
- We will be grateful to publishing of this manuscript in the Journal of Molecular Structure. 394
- 395
- 396
- 397





