

Pd(II), Pt(II), Zn(II), Cd(II) AND Hg(II) COMPLEXES OF THE NEWLY PREPARED 1,2-BENZOISOTHIAZOL-3(2H)-DITHIOCARBAMATE (BIT-DTC) LIGAND

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ABSTRACT. In the current work, we report the synthesis and characterization of new dithiocarbamate complexes derived from 1,2-benzisothiazol-3(2H)-one (BitH). The ligand was synthesized by treating the BitH with carbon disulfide in a basic solution. The NMR technique confirmed the preparation of the ligand. The treatment of the Bit-dtcNa with the metal salt's solution afforded the complexes of the type $[M(\text{Bit-dtc})_2]$; M = Zn, Cd, Hg, Pd, and Pt. The complexes were characterized via FT-IR and ¹H-NMR techniques. The Zn, Pd, and Pt complexes were investigated theoretically, and some of their quantum properties were determined. These parameters include HOMO-LUMO energies, electron affinity, ionization potential, chemical hardness, dipole moment and the total energies of the optimized structures. Moreover, the surface structure of Zn and Hg complexes were investigated by SEM and XRD techniques. The SEM pattern showed a cubic structures for the Zn complex while the Hg complex appeared as a nano rods structure. The calculated average particle sizes for Zn and Hg complexes were 23 and 26 nm, respectively.

KEY WORDS: Dithiocarbamate, 1,2-Benzisothiazol-3(2H)-one, DFT, SEM, XRD

INTRODUCTION

Dithiocarbamates are versatile ligands that are known to form stable complexes due to the electron delocalization of their (N-CSS-) group around the central metal (Figure 1). Dithiocarbamate ligands coordinate to transition and non-transition metal elements via its sulfur atoms in a mono- or bidentate mode. In the past two decades, complexes derived from dithiocarbamate have attracted more interest due to their diverse applications [1-3]. Palladium(II) and platinum(II) dithiocarbamate complexes of group 10 metal ions exhibited promising antimicrobial and anticancer properties [4, 5]. For instance, dithiocarbamate complexes of Pt(II) and Pd(II) are known to have potent cytotoxic effects against colon, lung, renal, ovarian, prostate, melanoma, and breast cancer. [6, 7]. In addition, the dithiocarbamate moiety as chelating agent has been increasingly utilized to treat heavy metal pollution [8]. For instance, Halawa *et al.* [9] demonstrated that dithiocarbamate ligands are more effective than activated carbon at removing heavy metal ions (Pb(II), Cd(II), Cu(II), and Zn(II)) from polluted water. Hou *et al.* [10] demonstrated that mercury(II) ion is efficiently precipitated upon treatment with dithiocarbamate moiety, which is a result of the dithiocarbamate ligand's high stabilizing effect. Furthermore, dithiocarbamate-based complexes have been used as single source precursors for sulfide nanoparticles [11-13] that show wide range of applications including: image sensors, photoelectric conversion devices, solar cells, ultrasonic transducers, flat-panel devices, and non-linear optical materials [14-19].

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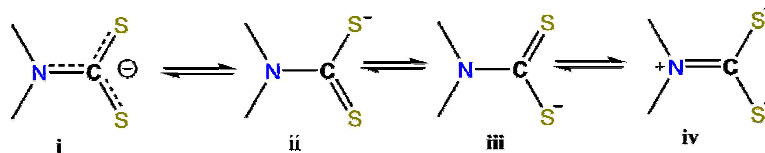


Figure 1. Resonance structures of dithiocarbamate ligand.

Benzisothiazolinone (Hbit) also known as 1,2-benzisothiazol-3(2H)-one is a heterocyclic ligand that is analogous to saccharin with N, S and O donor atoms (Figure 2). However, there is only few Bit-metal based complexes have been reported in the literature [20, 21]. Benzisothiazolinone can be deprotonated through its N-H amide group by a sodium hydroxide base. Al-Jibori's group has reported several N-bonded metal complexes derived from (Hbit) ligand [22-25]. Due to the weakly acidic nature of the amide proton, amide-derived dithiocarbamate ligands have not been extensively studied. Consequently, only a few instances have been reported in the literature [26].

In this study, we aimed to investigate the possibility of synthesizing metal-dithiocarbamate Hbit-derived complexes. We report the synthesis and characterization of the first benzisothiazolinone-dithiocarbamate ligand. In addition, a series of novel divalent metal ion complexes of Pd, Pt, Hg, Zn, and Cd derived from benzisothiazolinone-dithiocarbamate have been synthesized and characterized. Furthermore, using SEM and XRD techniques, we investigated the nanoparticle properties of some of the complexes described above.

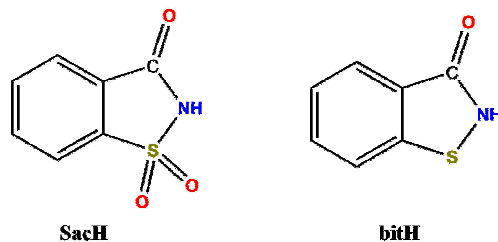


Figure 2. Saccharin (sacH) and benzisothiazolinone (bitH).

EXPERIMENTAL

Synthesis of the ligand

Sodium 1,2-benzisothiazol-3(2H)-dithiocarbamate (Bit-dtc) [32]. To an ice-cold solution mixture of 1,2-benzisothiazol-3(2H)-one (1 g, 6.615 mmol) in ethanol 20 mL and sodium hydroxide (0.265 g, 6.615 mmol), was added carbon disulfide (0.5 g, 6.615 mmol). The mixture was stirred at 0 °C for 30 min., and then it was allowed to stir at room temperature for 4 hours. The solution was allowed to slowly evaporate, resulting in the formation of white crystals (1.211 g).

(Bit-dtc-Na). White crystals. 1.211 g, 73% yield. Anal. calc. for $C_8H_4NOS_3Na$: C, 46.74; H, 2.62; N, 6.06. Found: C, 46.80; H, 2.61; N, 6.17%. IR (KBr, cm^{-1}): 3028 ν (C-H); 1639 ν (C=O); 1508 ν (C=N); 1058 ν (CSS). 1H NMR (DMSO- d_6 , δ ppm): δ 7.19 (*t*, $J_{HH} = 8.00$ Hz, H), 7.36 (*t*, $J_{HH} = 8.00$ Hz, H), 7.68 (*d*, $J_{HH} = 12.00$ Hz, H); 7.84 (*d*, $J_{HH} = 12.00$ Hz, H). ^{13}C NMR (DMSO- d_6 , δ ppm): δ 173.39 (C=S), δ 164.29 (C=O), δ 120.73-150.43 (aromatic ring).

Synthesis of the complexes (1-5)

General procedure. To a stirred an ethanolic solution of metal's salt (1 mmol) 10 mL was added a solution of Bit-dtc (2 mmol) in ethanol 10 mL which resulted in immediate white precipitate except for platinum(II) and palladium(II) where given brown and red precipitate respectively. The reaction mixture was stirred at room temperature for 3 hours, which was filtered-off, washed with distilled water and vacuum dried.

[Zn(Bit-dtc)₂] (1). White powder. 0.428 g, 82% yield. Anal. calc. for C₁₆H₈N₂O₂S₆Zn: C, 37.10; H, 1.65; N, 5.41. Found: C, 37.15; H, 1.59; N, 5.50%. IR (KBr, cm⁻¹) 3063 ν(=C-H); 1572 ν(C=O); 1496 ν(C-N); 1057 ν(CSS); ¹H NMR (DMSO-d₆, δ ppm): 7.43 (t, 1H, benzene ring), 7.61 (t, 1H, benzene ring), 7.94 (m, 2H, benzene ring).

[Cd(Bit-dtc)₂] (2). White powder. 0.508 g, 90% yield. Anal. calc. for C₁₆H₈N₂O₂S₆Cd: C, 34.01; H, 1.43; N, 4.96. Found: C, 34.08; H, 1.43; N, 4.99%. IR (KBr, cm⁻¹) 3057 ν(=C-H); 1568 ν(C=O); 1487 ν(C-N); 879 ν(CSS) ¹H NMR (DMSO-d₆, δ ppm): 7.28 (t, 1H, benzene ring), 7.47 (t, 1H, benzene ring), 7.79 (dd, 2H, benzene ring).

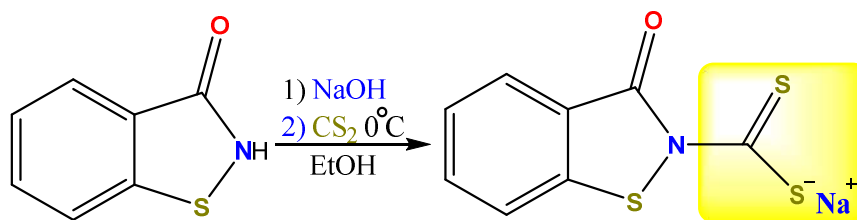
[Hg(Bit-dtc)₂] (3). White powder. 0.592 g, 91% yield. Anal. calc. for C₁₆H₈N₂O₂S₆Hg: C, 29.42; H, 1.23; N, 4.29. Found: C, 29.40; H, 1.19; N, 4.33%. IR (KBr, cm⁻¹) 3088 ν(=C-H); 1579 ν(C=O); 1556 ν(C-N); 939 ν(CSS) ¹H NMR (DMSO-d₆, δ ppm): 7.37 (t, 1H, benzene ring), 7.61 (t, 1H, benzene ring), 7.86 (dd, 2H, benzene ring).

[Pd(Bit-dtc)₂] (4). Red powder. 0.489 g, 87% yield. Anal. calc. for C₁₆H₈N₂O₂S₆Pd: C, 34.38; H, 1.44; N, 5.01. Found: C, 34.35; H, 1.41; N, 5.12%. IR (KBr, cm⁻¹) 3061 ν(=C-H); 1633 ν(C=O); 1483 ν(C-N); 889 ν(CSS) ¹H NMR (DMSO-d₆, δ ppm): 7.15 (t, 1H, benzene ring), 7.31 (t, 1H, benzene ring), 7.58 (d, H, benzene ring), 7.62 (d, H, benzene ring).

[Pt(Bit-dtc)₂] (5). Brown powder. 0.468 g, 72% yield. Anal. calc. for C₁₆H₈N₂O₂S₆Pt: C, 29.76; H, 1.25; N, 4.33. Found: C, 29.75; H, 1.21; N, 4.38%. IR (KBr, cm⁻¹) 3063 ν(=C-H); 1631 ν(C=O); 1585 ν(C-N); 914 ν(CSS) ¹H NMR (DMSO-d₆, δ ppm): 7.26 (m, 1H, benzene ring), 7.44 (m, 1H, benzene ring), 7.70 (m, 2H, benzene ring).

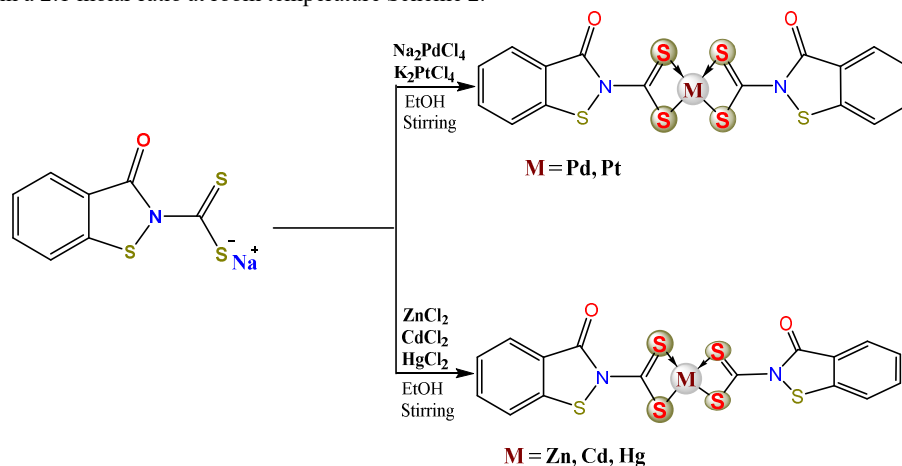
RESULTS AND DISCUSSION

The ligand Bit-dtc was synthesized by simply mixing an equimolar amount of 1,2-benzisothiazol-3(2H)-one and carbon disulfide in the presence of sodium hydroxide under ice-cold conditions. The resulting solution was left for slow evaporation, which yielded white crystals 1. 211 g, 73% yield (Scheme 1).



Scheme 1. Synthesis of sodium 1,2-benzisothiazol-3(2H)-dithiocarbamate.

The IR and NMR data supported the formation of the dithiocarbamate ligand. The complexes (**1-5**) were prepared by mixing the dithiocarbamate ligand's solution and the metal's salt solution in a 2:1 molar ratio at room temperature Scheme 2.



Scheme 2. General route for the synthesis of (**1-5**) complexes.

All of the synthesized complexes were characterized by IR and NMR techniques.

IR spectra

The IR spectrum of the ligand Bit-dtc showed the absence of $\nu(\text{N-H})$ absorption band at 3200 cm^{-1} . Also, the $\nu(\text{C=S})$ stretching band showed at 1058 cm^{-1} . Strong absorption band showed at 1570 cm^{-1} that is attributed to $\nu(\text{C-N})$ stretching band. The dithiocarbamate group CSS is expected to coordinate through both of their sulfur atoms in a bidentate fashion. The $\nu(\text{C-S})$ appear within $1100\text{-}980\text{ cm}^{-1}$ range that attributed to the bidentate behavior [34].

Finally, the IR absorption bands that associate with metal-sulfur bond are expected to show between $425\text{-}500\text{ cm}^{-1}$ [34] except for cadmium, which shows around $620\text{-}650\text{ cm}^{-1}$ [35].

^1H and ^{13}C NMR spectra

The $^1\text{H-NMR}$ chart of the newly prepared ligand (Bit-dtc) shows the absence of the amide proton while it displays four separate peaks that correspond to the protons of the benzene ring (Figure 3). For instance, the protons numbered H1 and H4 display as two doublets at 7.84 ppm (d, 1H) and 7.68 ppm (d, 1H) respectively. In addition, the protons H3 and H2 show as two separate triplets at 7.36 ppm (t, 1H) and at 7.19 ppm (t, 1H), respectively.

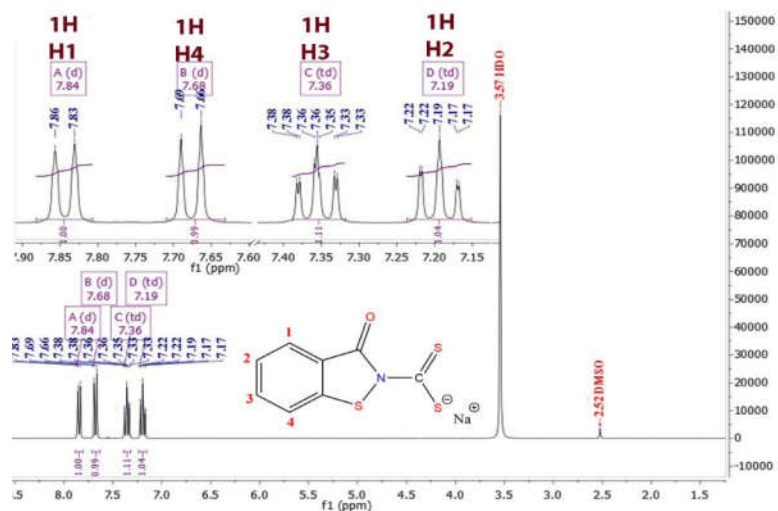


Figure 3. The ^1H -NMR chart for the ligand Bit-dtc.

The ^{13}C - $\{^1\text{H}\}$ -NMR spectrum of the mother ligand showed the newly attached thiocarbonyl moiety which appears at 173 ppm. Moreover, the carbonyl group shows at 164 ppm, which resembles its (bitH) derivatives [26]. Finally, the benzene carbon ring shows as expected which displays at 150, 130, 126, 124, 122, and 120 ppm corresponding to the carbon atoms numbered C4, C3, C6, C2, and C5, respectively (Figure 4).

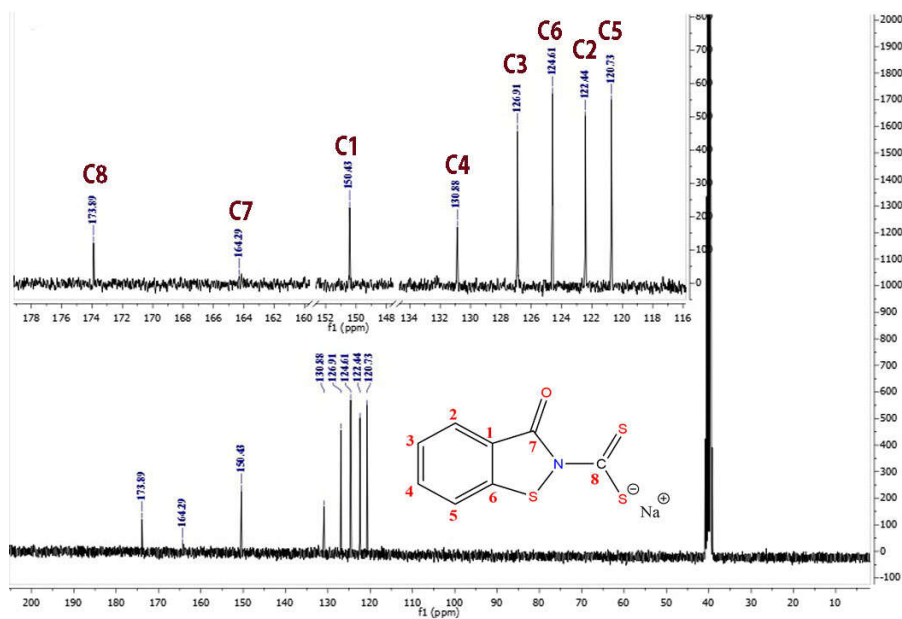


Figure 4. The ^{13}C -NMR chart for the ligand Bit-dtc.

DFT analysis

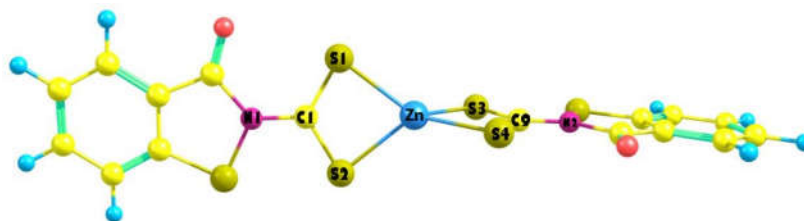
The geometries of the obtained complexes were optimized via Gaussian 09 W at B3LYP method by utilizing SDD basis set for Zn, Pd and Pt metal ions, and 6-311 G(d,p) basis set for the ligand (Bit-dtc). Chemcraft and GaussView visualized the optimized complexes. There are different parameters that have been evaluated. For instance, the energies of the HOMO-LUMO orbitals were determined. In addition, the values of electron affinity, ionization potential, chemical hardness, dipole moment and the total energies of the optimized structure were calculated.

Geometric structures investigation

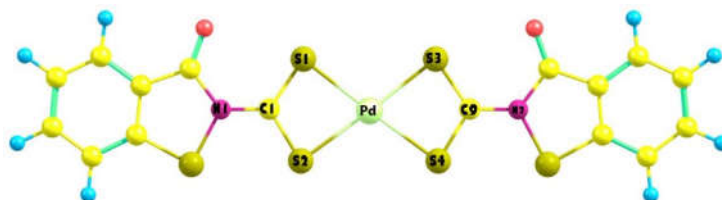
The optimized structures of complexes 1, 4 and 5 were examined and compared to the reported values [27-30]. As expected, the zinc(II) complex showed tetrahedral geometry while complexes of palladium(II) and platinum(II) showed square planar geometry.

The calculated C-S distance showed equal values for both of the C-S bonds in the CSS moiety. In addition, the C1-N1 and C9-N2 distances appear shorter than expected. Therefore, a single bond character between the carbon and nitrogen atoms is not a proper description but rather a semi-double bond characteristic. These results are consistent with the experimental ones, which reflect a resonance structure between both the C-S bonds and the C1-N1 bond. The bond angles for complexes 4 and 5 show a square planar Pd(II) and Pt(II) complexes.

Chemical reactivity is the propensity of two substances to engage in a chemical reaction. The chemical reactivity of a molecule relies on the energy gap between its HOMO and LUMO orbitals [36]. Hence, the Pt(II) complex is anticipated to be the most reactive and softer chemical compared to the other two complexes. The reactivity of the Pd(II) complex is greater than that of the Pt(II) complex. The Zn(II) complex is anticipated to have the maximum reactivity. The hardness values are determined using the formula $\frac{1}{2} (E_{\text{LUMO}} - E_{\text{HOMO}})$. High value indicates resistance to charge transfer and reactivity [37]. Pt(II) complex can experience changes in electron density more readily than Pd(II) and Zn(II) complexes. Electronegativity (LE) is a measure of a molecule's capacity to attract electrons in a covalent connection. The Zn(II) complex has a higher electronegativity value of 6.45 eV compared to the Pt(II) and Pd(II) complexes. Meaning, it is best electron acceptor than other complexes [38]. The dipole moment of the synthesized compounds exhibit similar values, as anticipated.



(i)



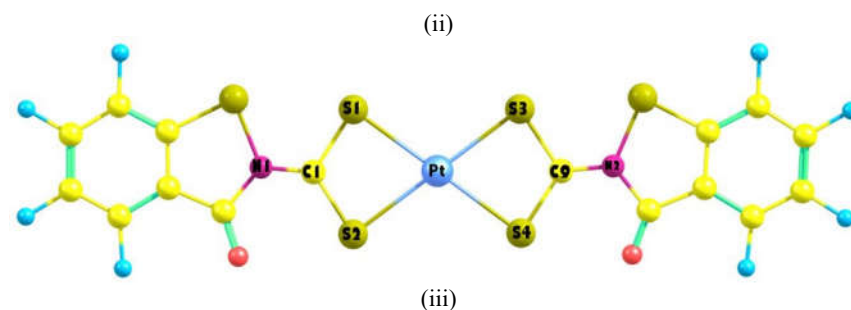


Figure 5. Optimized structure of i) [Zn(Bit-dtc)₂], ii) [Pd(Bit-dtc)₂], and iii) [Pt(Bit-dtc)₂].

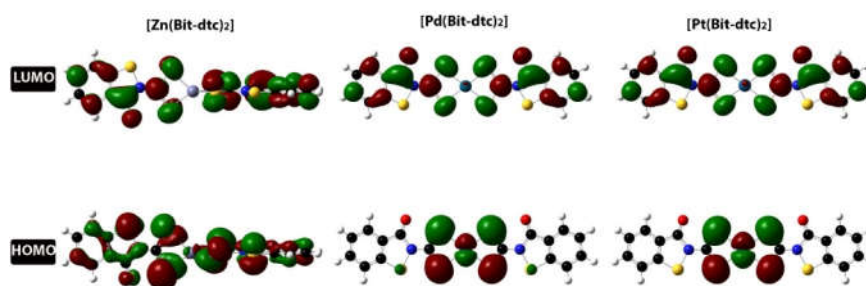
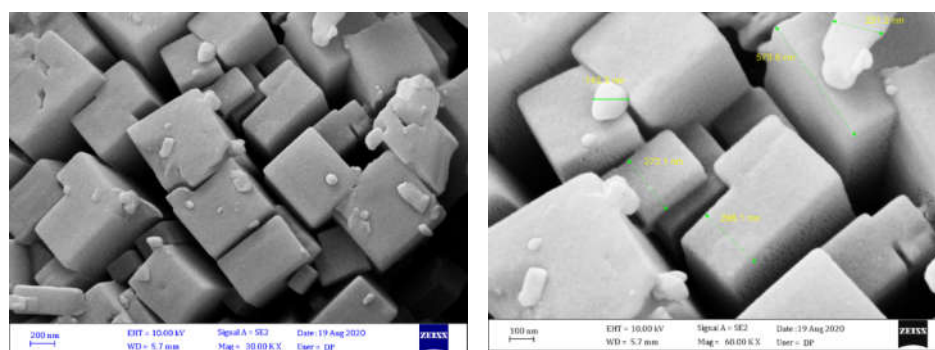


Figure 6. The HOMO and LUMO orbitals for [Zn(Bit-dtc)₂], [Pd(Bit-dtc)₂], and [Pt(Bit-dtc)₂].

SEM and XRD data analysis

The SEM images of the complexes 1 and 3 showed two different patterns. For instance, the mercury complex appeared as nano-rods with a thickness of 107 – 555 nm, while the complex of zinc showed a nano-cubic structure with thickness of 143 – 570 nm.



a) [Zn(Bit-dtc)₂]

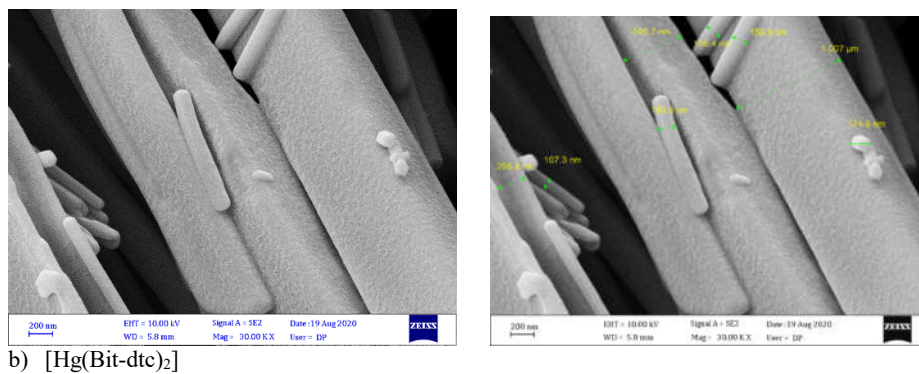


Figure 7. The SEM images for complexes of a) $[\text{Zn}(\text{Bit-dtc})_2]$ and b) $[\text{Hg}(\text{Bit-dtc})_2]$.

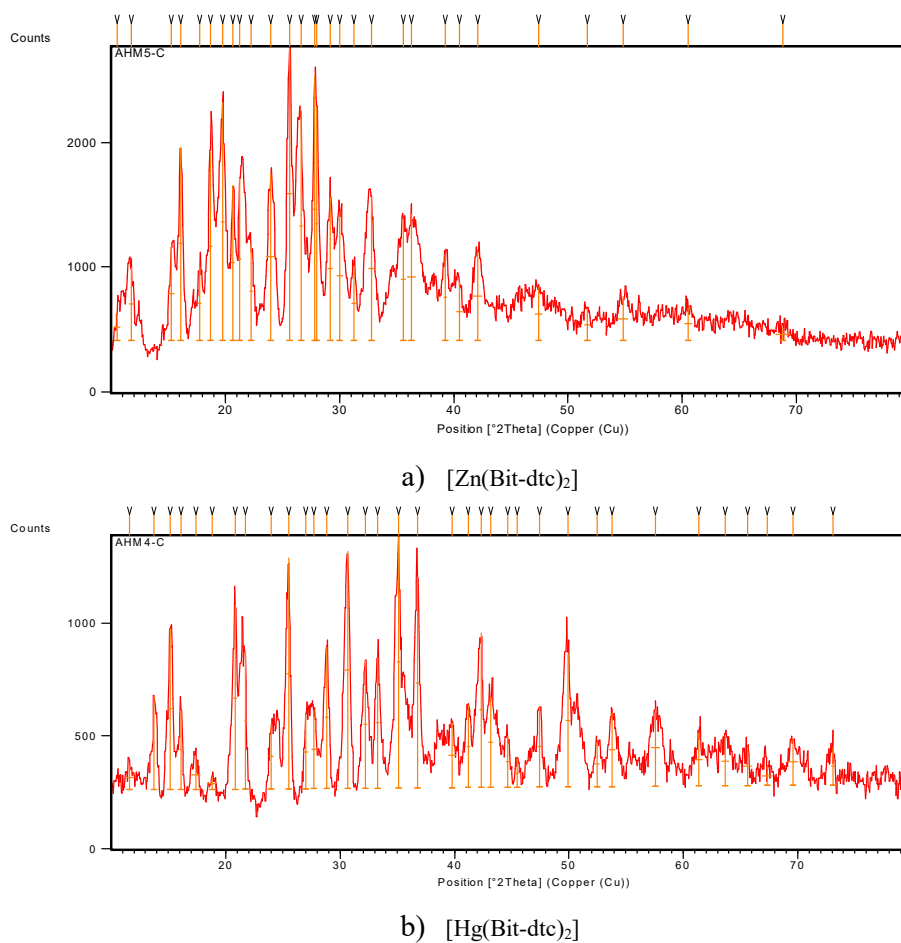


Figure 8. The XRD charts for complexes of a) $[\text{Zn}(\text{Bit-dtc})_2]$ and b) $[\text{Hg}(\text{Bit-dtc})_2]$.

The X-ray diffraction of the powder has been determined for complexes 1 and 3. Both of mercury and zinc complexes showed multiple peaks that are overlapped with each other, within 10 – 75 range and 10 – 60 range, respectively. The overlapping peaks are attributed to the amorphous characteristic of these complexes [31]. With the help of the Deby-Scherre equation [$B = 0.94\lambda / (S \cos \theta)$], the particle sizes were calculated. Symbols like B represents FWHM (the full width at half maximum), while θ and S the angles of diffraction and crystal size, respectively.

CONCLUSION

Upon treating the 1,2-benzisothiazol-3(2H)-one (BitH) with carbon disulphide in the presence of NaOH, it gave the first 1,2-benzisothiazol-3(2H)-dithiocarbamate ligand (Bit-dtc). This ligand was characterized by different spectroscopic methods and its structure was determined with high accuracy. A series of metal complexes derived from (Bit-dtc) were simply obtained by reacting two moles of the ligand with one mole of the metal's salt. The obtained complexes were investigated in terms of their quantum parameters and their structural characteristic using SEM and XRD techniques. The theoretical calculations showed that there is an equal electronic distribution along the N-CSS moiety, which suggests a resonance structure between these atoms. While the SEM and XRD data suggest that Zn and Hg complexes are both amorphous in nature.

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