Asian Journal of Chemistry; Vol. 34, No. 11 (2022), 2833-2838

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2022.23841

Synthesis, Spectroscopic, DFT, HOMO-LUMO, MEP, Mulliken Analysis and Antimicrobial Properties of Novel Arsenic(III) Dithiocarbamate Complex

SUNDARAMOORTHY TAMILVANAN

Department of Chemistry, Annamalai University, Annamalainagar-608002, India

Corresponding author: E-mail: laksuntam@gmail.com

Received: 20 March 2022; *Accepted*: 24 June 2022; *Published online*: 19 October 2022; AJC-20993

The novel arsenic dithiocarbamate complex was synthesized and characterized by elemental analysis, NMR and FTIR. Density functional theory (DFT) was used to calculate quantum mechanical computations of a *tris*(N,N-difurfuryldithiocarbamato)arsenic(III) molecule employing the standard B3LYP basis set with the GAUSSIAN 09 program. The molecular structure was confirmed using geometrical parameters, vibrational analysis (FT-IR), ^{13}C NMR and ^{1}H NMR (GIAO technique). The HOMO-LUMO energy gap, Mulliken population analysis, contour map and molecular electrostatic potential (MEP) surfaces have all been determined using molecular orbital calculations. The minimal HOMO-LUMO energy values shows that charge transfer is possible within the molecule. Gram-positive and Gram-negative bacteria, as well as fungal species, were used to investigate the compound antimicrobial susceptibility. The results demonstrated that even at high concentrations, the complex was effective against the microorganisms.

Keywords: Dithiocarbamate, Arsenic complexes, Antimicrobial activity, Molecular electrostatic potential.

INTRODUCTION

Dithiocarbamates or carbamodithioates are compounds possessing the dithiocarbamate group as a functional group ($N-CS_2$) is the general formula for compounds. Because of their phytoalexin, brassinin, which was initially discovered in cabbage [1], they are fascinating chemical substances. Because of its chemopreventive and anticancer properties, brassinin can be obtained from cauliflower, broccoli and lettuce [2]. The chemistry of As(III) dithiocarbamates has attracted a lot of attention in the past few decades [3,4]. It was inspired by either their prospective applications (*e.g.* fungicides, desiccants, herbicides and wood preservatives) or their fascinating structural behaviour arising from the different coordination patterns of the dithiocarbamate ligands [5].

The inhibitory effect of arsenic(III) dithiocarbamates on enzyme activity is a well-studied biochemistry phenomenon [6-8]. Arsenic is cytotoxic and the ability of arsenite [As(III)] to bind protein thiols is thought to be the mechanism of toxicity. It can potentially damage chromosomes and prevent DNA repair [9]. When dithiocarbamate ligands are coordinated to main group elements, the structural properties of the ligands do not change considerably. Dithiocarbamates have been used in biological investigations for anticancer [10], antibacterial [11], antifungal [12], growth depressing [13], rodent-repelling [14] and toxicity studies [15]. According to Manav *et al.* [14] Pd(II) and Pt(II) complexes of dithiocarbamates have attracted a lot of interest because they have better anticancer, antitumor and less toxic characteristics than cisplatin [16]. Over the past years, several authors have reported the usefulness of many derivatives of dithiocarbamates as antimicrobial agents [17-19]. Herein, we reported the synthesis, characterization and antimicrobial activity of *tris*(N,N-difurfuryldithiocarbamato)-arsenic(III), a new dithiocarbamte complex. Density functional theory studies were also carried out on the synthesized arsenic dithiocarbamate complex.

EXPERIMENTAL

The analytical grade chemicals *viz.* arsenic(III) chloride, furfurylamine, furfuraldehyde and the solvents were used without any purification. On thermal melting point equipment, melting points were obtained in open capillary tubes. Elemental studies (CHN) were performed at a Sophisticated Analytical Instrument Facility Center, CDRI, Lucknow, India, by Elementar

Analyse Systeme Gmbh Vario El V3.00. A KBr disc was used to record the infrared spectrum on a Thermo Shimadzu FT-IR spectrophotometer in the region of 4000-400 cm^{-1}. The ^{1}H & ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively, using a Bruker 400 MHz spectrometer. The chemical shifts were measured in parts per million (ppm) with respect to an internal standard, TMS.

Synthesis of secondary amines: In methanol, furfuraldehyde was added to furfurylamine and mixed thoroughly for 2 h. The removal of solvent was done by evaporation. The resulting oily product was dissolved in a solvent mixture of methanol and dichloromethane. At 5 ºC, sodium borohydride was gradually added and swirled for 2 h. At room temperature, the reaction mixture was stirred again for 12 h. The resulting viscous liquid was washed with water and dichloromethane was used to extract the product after the solvent was evaporated. A secondary amine based on furfuryl was obtained [20].

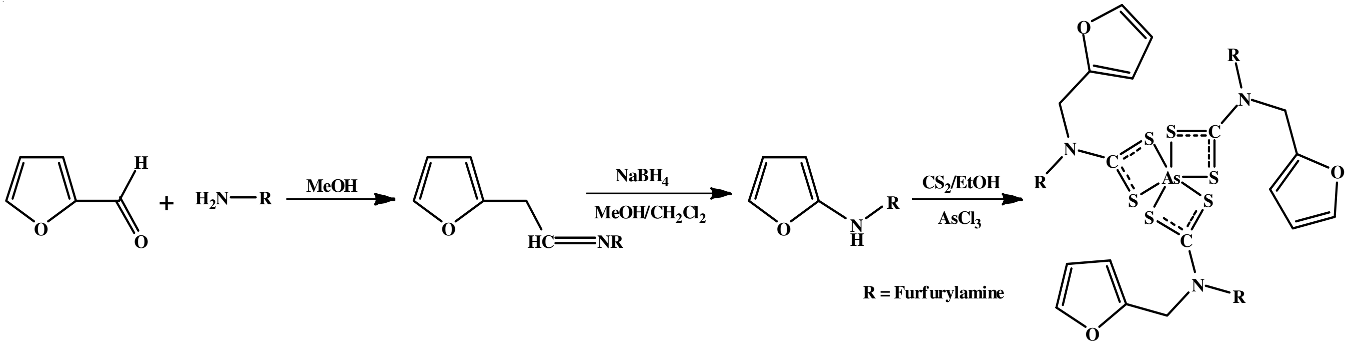
Synthesis of *tris*(N,N-difurfuryldithiocarbamato)-arsenic(III) complex: In ethanol, furfuryl based secondary amine and CS_2 were dissolved and the reaction mixture was swirled for 30 min at ice cold temperatures. The solution was then added to $AsCl_3$ solution. Filtration was used to obtain the yellowish solids, which were then washed and dried. To obtain the excellent yield, the obtained product was recrystallized (**Scheme-I**). Yield: 79%, m.p.: 171 ºC. Anal. calcd. (found)% for $C_{33}H_{30}N_3O_6S_6As$ (*m.w.* 831.92): C, 47.64 (47.59); H, 3.63 (3.61); N, 5.05 (5.00). IR (KBr, cm^{-1}): Experimental: 1443 ν(C-N), 1009 ν(C-S), 2900 ν(C-H); Theoretical: 1456.17 ν(C-N), 981.69 ν(C-S), 3062.25 ν(C-H). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): Experimental: 5.09 (12H, s, CH_2 furfuryl); 6.28 (6H, H-4 (furyl); 6.39 (6H, H-3, (furyl); 7.35 (6H, H-5 (furyl): Theoretical: 5.0596 (69H) (CH_2 furfuryl); 5.6133 (71H) (6H, (furyl); 5.8751 (72H) (6H, (furyl); 7.21655 (73H) (6H, (furyl): ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): Experimental: 47.9 (CH_2 furfuryl carbons); 110.2, 110.4, 143.2, 141.5 furyl ring carbons); 202.9 (NCS_2): Theoretical: 44.4472 (24C) (CH_2 furfuryl carbons); 103.1921 (27C), 105.7319 (26C), 141.7187 (28C), 151.0340 (27C) furyl ring carbons); 233.6852 (23C) (NCS_2).

Computation studies: The optimized structural computations were carried out using B3LYP in association with LANL2DZ basis sets using Gaussian 09W without symmetry requirements [21]. Gaussian 09 W was used to determine the majority of the optimized structural parameters, such as bond distance, bond angle and dihedral angle. A number of programs, particularly Gauss View, have been used to investigate the infrared spectrum. The ^{1}H & ^{13}C NMR spectra were obtained using the GIAO [22] techniques at DFT with $CDCl_3$ as the solvent and TMS as standard reference. The Gauss View 5.0 was used to calculate the energy gap, global softness (S), energy gap, electronegativity (χ), chemical potential (μ), electrophilicity index (ω) and global hardness (η) of systems. At a similar level of theory, the molecular electrostatic potential (MEP) mapping, contour map, HOMO, LUMO and Mulliken charge distribution of atoms were examined. Other characteristics such as molecule dipole moment and total energy were also calculated.

Antimicrobial activity: Mueller Hinton Agar-well diffusion technique [23] was used to incubate microorganism cultures (*Escherichia coli*, *Staphylococcus aureus*, *Klebsiella pneumoniae*, *Vibrio cholerae*, *Candida albicans* and *Aspergilus niger*). The test microorganism cultures were prepared in a sterile nutrient broth medium and cultured for 24 h at 37 ºC for bacteria and 27 ºC for fungal cultures. On the spread plates, a sterile antimicrobial disc (6 mm in diameter) was loaded with varying concentrations (400 and 800 µg/mL) of complex. For 24 h, the spread plates were incubated. After that, the zones of inhibition were investigated and the activity against the pathogens tested was measured. The reference drug in this study was ciprofloxacin.

RESULTS AND DISCUSSION

Infrared studies: The synthesized arsenic dithiocarbamates have three distinct bands in their IR spectra (Fig. 1), which are mostly associated with the stretching vibrational bands. For all metal complexes, the ν(C-S) stretching vibration (1050-950 cm^{-1}) is shown as distinct bands, indicating a symmetrical bonding of the ligand's S atoms to the central metal ion. The ν(C-S) stretching vibration band was obtained at 1009 cm^{-1}, whereas the computational calculation band was obtained at 981.69 cm^{-1} using the B3LYP theoretical method. The arsenic dithiocarbamate complex C-N (thioureide) stretching bands (1550-1450 cm^{-1}) appeared as broad bands. For arsenic dithiocarbamate complex, the thioureide ν(C-N) band was observed at 1443 cm^{-1}, which was computationally calculated as 1456.17 cm^{-1}. The aromatic ν(C-H) band was obtained at 2900 cm^{-1}. This band is a feature of the NCS_2 band with an intermediary bond between the single bond (1350-1250 cm^{-1}) and the double bond (1690-1640 cm^{-1}).



Scheme-I: Preparation of the complex

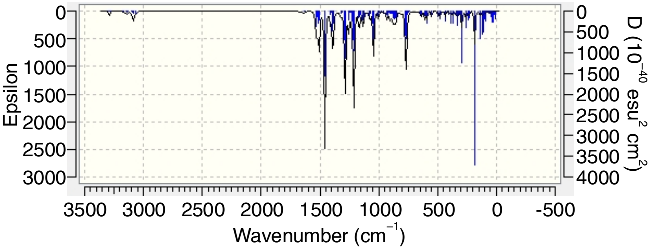


Fig. 1. Theoretical infrared spectrum of the complex

NMR studies: The singlet observed at δ 5.09 ppm for the arsenic complex was assigned to CH_2 protons for the furfuryl group, which gave the signal of δ 5.0596 ppm based on the computational spectrum. When compared to the proton on the parent amine, the N-CH_2 (furfuryl) signals were moved significantly downfield (Fig. 2). The aromatic proton signals were found in the downfield in the range of δ 6.28-7.35 ppm, which corres-ponded to theoretical values of δ 5.61325-7.21655 ppm. The NCS_2 thioureide carbon signals were in the expected range for dithiocarbamate complexes (~δ 200 ppm) [24]. The thioureide carbon appeared at δ 202.9 ppm in arsenic complex signals employing the gauge-invariant atomic orbital (GIAO) approach, which was observed at δ 233.6852 ppm in the theoretical spectra. The signal for furfuryl's CH_2 carbon occurs at δ 47.9 ppm, which correlates to a theoretical value of δ 44.45 ppm. A downfield shift of CH_2 carbon signals compared to similar carbons in the parent amine indicates that the complexation process has a significant effect.

Optimized structure: The optimized molecular structure of the synthesized arsenic dithiocarbamate complex (Fig. 3) had energy (-1957.446051 au) and dipole moment (4.0332 eV). The bond length, bond angle and dihedral angle for the dithiocarbamate complex were determined using the optimal molecular structural parameters. Table-1 shows the computed selected geometric properties of the title molecule *tris*(N,N-difurfuryldithiocarbamato)arsenic(III). The C-N and C-S bond lengths in the complex's structure were 1.3558-1.3592 (C12-N35, C1-N34 and C23-N36) and 1.7399-1.8386 (C12-S45, C23-S47, C1-S44, C1-S43, C23-S48 and C12-S46), respectively. The short thioureide C-N bond lengths range from 1.3558 to 1.3592 Å, indicating delocalized electron density over the S_2CN moiety and the partial double bond character of this complex. The C–S distances (mean: 1.78805 Å) indicate partial double bond characters and are an intermediate value between single and double bond distances. The arsenic dithiocarbamate complex's bond angle and torsional angle were determined to be -175.9811° (S44-C1-N34-C2) and 57.5789° (H69-C24-C25-O41), respectively.

Frontier molecular orbitals (FMOs): The polarizability, chemical hardness, reactivity and softness values of a molecule can be computed by using the energy difference between the highest occupied molecular orbital and the lowest unoccupied molecular orbital and the calculated energy gap value was found to be 3.7638 eV . It is likely that HOMO performs as a Lewis base and help in an oxidation reaction. As shown in Table-2, the values of electron affinity (EA) and ionization

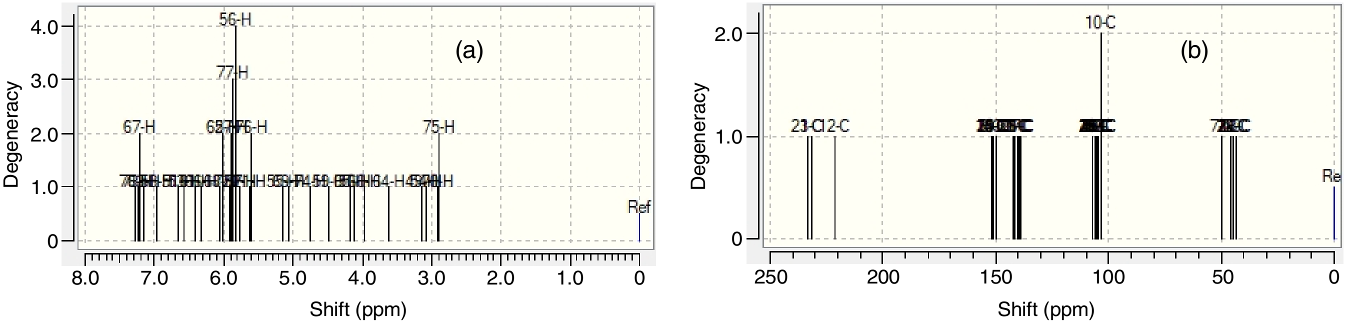


Fig. 2. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of the complex

TABLE-1
SELECTED BOND LENGTH (Å), BOND ANGLE (°) AND DIHEDRAL ANGLES (°) OF THE COMPLEX

Bond distances (Å)		Bond angles (°)		Dihedral angles (°)	
S43-As79	2.6584	S43-As79-S44	67.0114	S43-C1-N34-C2	2.6546
S44-As79	2.8756	S47-As79-S48	67.0914	S43-C1-N34-C7	176.2897
S45-As79	3.061	S45-As79-S46	67.0878	S44-C1-N34-C2	-175.9811
S46-As79	2.4481	S47-C23-S48	117.6333	N34-C1-43 -As79	177.4377
S47-As79	2.8711	S47-C23-N36	122.8818	S44-C1-S43-As79	-3.8499
S48-As79	2.6531	S48-C23-N36	119.4838	N34-C1-S44-As79	-177.7742
C23-N36	1.3592	C24-N36-C29	115.2864	H56-C9-C10-C11	-179.5701
C23-S47	1.7661	S45-C12-S46	119.1916	H56-C9-C10-H57	0.1195
C23-S48	1.8084	S45-C12-N35	124.3984	C9-C10-C11-O38	-0.425
C12-N35	1.3558	S46-C12-N35	116.41	C9-C10-C11-H58	179.3981
C12-S45	1.7399	C18-N35-C13	115.0317	N36-C24-C25-C26	120.7715
C12-S46	1.8386	S43-C1-S44	117.7217	N36-C24-C25-O41	-62.9748
C1-N34	1.357	S43-C1-N34	118.927	H69-C24-C25-C26	-118.6748
C1-S43	1.8083	S44-C1-N34	123.3378	H69-C24-C25-O41	57.5789

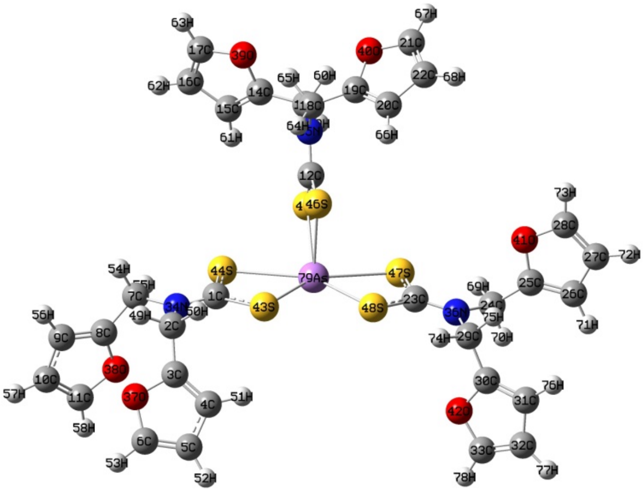


Fig. 3. Optimized geometry of the complex

TABLE-2
CALCULATED CHEMICAL PARAMETERS OF THE COMPLEX

Parameters	Theoretical values (eV)
HOMO	-5.6876
LUMO	-1.9238
Energy gap	3.7638
Ionization potential (IP)	5.6876
Electron affinity (EA)	1.9238
Global hardness (η)	1.8819
Chemical potential (μ)	-3.8057
Electronegativity (χ)	3.8057
Global softness (S)	0.2657
Electrophilicity Index (ω)	3.8481
Energy	-1957.446051 au
Dipole moment (Debye)	4.0332

potential (IP) can be used to determine these variables. According to Koopman's theorem [25], the ionization potential (IP) and electron affinity (EA) were represented as $IP = -E_{HOMO} = 5.6876$ eV and $EA = -E_{LUMO} = 1.9238$ eV, respectively. For the complex, the global hardness (η) and global softness (S) variables were [$\eta = \frac{1}{2}(E_{LUMO} - E_{HOMO}) = 1.8819$ eV] and ($S = 1/2\eta = 0.2657$ eV), respectively. According to the results, the dithiocarbamate complex is the least polarizable, hardest and least reactive of the molecules examined.

In the gas phase, the title molecule's electrophilicity index value of 3.8481 eV provides the substantial energy transformation between HOMO and LUMO. By using DFT/B3LYP with LANL2DZ as a basis set, the values of global hardness (η), chemical potential (μ), electronegativity (χ), global softness (S) and electrophilicity index (ω) for the title complex in the gas phase were 1.8819 eV, -3.8057 eV, 3.8057 eV, 0.2657 and 3.8481 eV, respectively. The electrophilicity index (ω) is a measure of energy loss due to the maximal electron flow between the acceptor and donor.

Molecular electrostatic potential (MEP): The DFT computations were used to determine the MEP surface analysis of the complex using the optimized structure and B3LYP theory parameters using the LANL2DZ base set. The MEP energy provides information about a molecule's charge distribution. A complex reactive site for nucleophilic and electrophilic attacks is shown in Fig. 4a. The reactive sites are positioned by specific colour codes in molecular electrostatic potential analysis. The charge-related properties and charge distribution of molecules can be visualized using a molecular electrostatic potential map. The electron-rich site, a negative area with electrophilic reactivity, is indicated by the red colour in MEP graphic. The MEP map's blue colour denotes an electron-deficient zone, which is a positive region with nucleophilic reactivity. The electrical potential of molecules increases in the order of red < orange < yellow < green < blue. Different colours, such as green, yellow and orange, are used to illustrate the areas between positive and negative potential. The range between -4.758 e^{-2} (red) and +4.758 e^{-2} (blue) in the complex is used to colour encode molecule electrostatic potential maps. The negative potential sites were often located in the area of an electron-rich zone. As can be observed in the negative, a region was mostly concentrated over the oxygen and nitrogen portions, indicating a potential site for the electrophilic reactions. The hydrogen atoms have an exceptionally large maximum positive

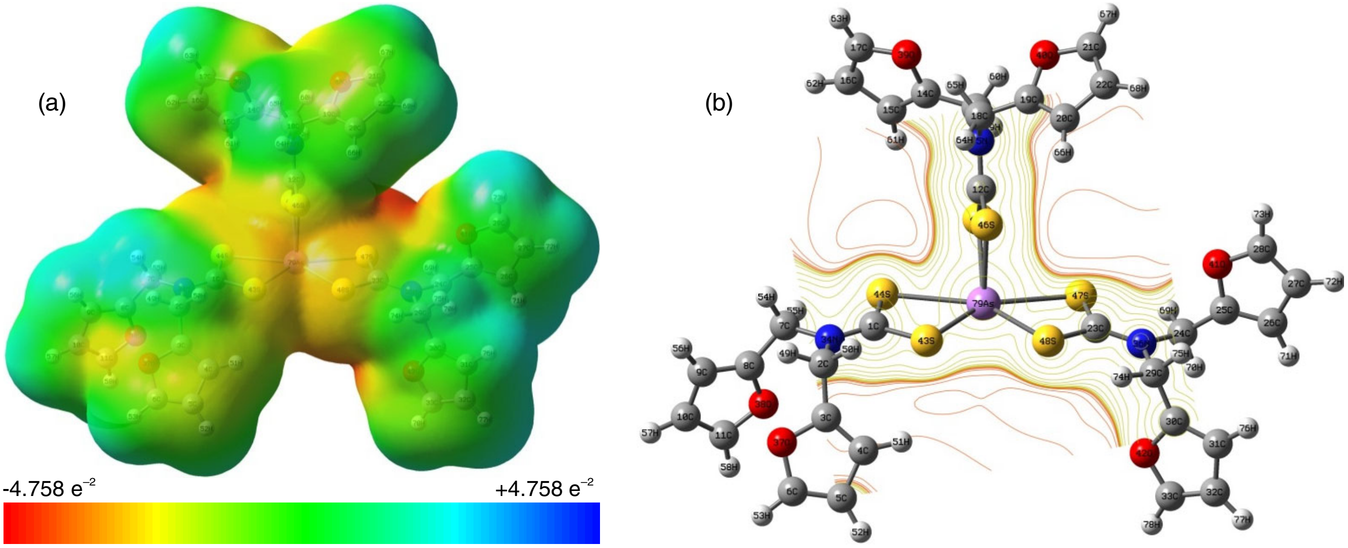


Fig. 4. MEP surface (a) and contour map (b) of the complex

area, indicating an appropriate site for the nucleophilic attack. The molecule's depletion zone had neither a positive nor a negative potential atom. The electron rich lines (red) are located near oxygen and nitrogen, whereas the electron deficient lines (greenish-yellow) are located around oxygen and nitrogen (Fig. 4b).

Mulliken atomic charges: The Mulliken population study uses DFT/B3LYP methods with a LANL2DZ basis level to compute the atomic charges on the atoms. Fig. 5 shows a graphical representation of the Mulliken charge distribution, with values reported in Table-3. For the title complex, there are a total of 79 atoms. It is noticed that all oxygen atoms have closed contours, as do each of the furfuryl rings. Since, electron withdrawing groups such as oxygen and nitrogen atoms are present near these atoms, the net positive charge of H66 = 0.273365, H61 = 0.275412 and H51 = 0.285633 atoms is greater than that of the other atoms. On 33 carbon atoms, the Mulliken charge distribution was either negative (C18 = -0.5018) or positive (C8 = 0.445552). These numbers revealed the nature of the meticulous atoms and their effect on the molecule's vibratory frequencies. The greatest positive charge of an arsenic atom is As79 = 0.590793.

Antimicrobial activity: Antimicrobial activity was tested against four bacterial species and two fungus species at the concentrations of 400 and 800 μg/mL. Table-4 summarizes the complex inhibitory actions against bacteria and fungi. According to the results of the disc diffusion method, the antibacterial effects of the coordinated As(III) atom were increased. The effect is proportional to the concentration of the complex, as indicated. The synthesized As(III) complex has less antibacterial activity against *Klebsiella pneumoniae* and higher antibacterial activity against *Vibrio cholerae* than other microorganisms. Antifungal investigations found that *Aspergillus niger* has better activity than *Candida albicans*. The antibacterial and antifungal activities of As(III) dithiocarbamate complexes were unaffected by the functionalization of N-bound organic moiety of dithiocarbamate ligand.

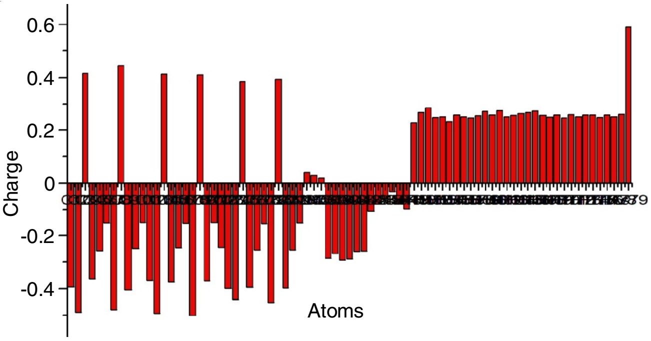


Fig. 5. Mulliken's plot of the complex

Conclusion

The structural elucidation of newly synthesized *tris*(N,N-difurfuryldithiocarbamato)arsenic(III) complex was carried out using various physico-chemical methods such as elemental analysis, melting point, IR, ^{1}H & ^{13}C NMR, theoretical studies and antimicrobial activities of As(III) complex have also been

TABLE-3
CHARGE DISTRIBUTION CALCULATED BY THE MULLIKEN ATOMIC CHARGE

Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge
C1	-0.393775	C21	-0.150715	O41	-0.2598	H61	0.275412
C2	-0.489495	C22	-0.244517	O42	-0.258388	H62	0.251011
C3	0.415759	C23	-0.399363	S43	-0.106211	H63	0.256057
C4	-0.364633	C24	-0.442	S44	-0.079844	H64	0.263895
C5	-0.256928	C25	0.385736	S45	-0.059349	H65	0.267239
C6	-0.151645	C26	-0.395741	S46	-0.033904	H66	0.273365
C7	-0.479244	C27	-0.254129	S47	-0.078347	H67	0.257105
C8	0.445552	C28	-0.153819	S48	-0.097506	H68	0.249724
C9	-0.404592	C29	-0.452765	H49	0.229711	H69	0.258781
C10	-0.248229	C30	0.393763	H50	0.268561	H70	0.247801
C11	-0.150504	C31	-0.397416	H51	0.285633	H71	0.259862
C12	-0.370018	C32	-0.254103	H52	0.248119	H72	0.251932
C13	-0.493976	C33	-0.151702	H53	0.251452	H73	0.258335
C14	0.41329	N34	0.03953	H54	0.234143	H74	0.258295
C15	-0.375498	N35	0.028219	H55	0.2588	H75	0.249252
C16	-0.245736	N36	0.018279	H56	0.251885	H76	0.258822
C17	-0.152755	O37	-0.286047	H57	0.247602	H77	0.251886
C18	-0.5018	O38	-0.267176	H58	0.255851	H78	0.260886
C19	0.410904	O39	-0.29219	H59	0.27212	As79	0.590793
C20	-0.371399	O40	-0.288919	H60	0.258812	–	–

TABLE-4
ANTIMICROBIAL ACTIVITY (DIAMETER OF INHIBITION ZONE) OF THE COMPLEX

	Disc content (μg)	Selected bacteria				Selected fungal	
		V. cholera	*S. aureus*	*K. pneumoniae*	*E. coli*	*C. albicans*	*A. niger*
Complex	400	9	6	5	7	8	10
	800	15	11	10	13	14	16
Ciprofloxacin (std. drug)		30	35	30	35	30	35

evaluated. The DFT studies at B3LYP/LANL2DZ basis set were calculated the FT-IR, NMR (GIAO method), FMOs, energy gap, bond lengths, bond angles, dihedral angles and various other parameters for the optimized molecule. The biological activities of arsenic(III) dithiocarbamate complexes were unaffected by the functionalization of N-bound organic moiety of dithiocarbamate ligand.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. A.T. Odularu and P.A. Ajibade, *Bioorg. Chem. Appl.*, **2019**, 8260496 (2019); https://doi.org/10.1155/2019/8260496
2. D. Ramirez, A. Abellán-Victorio, V. Beretta, A. Camargo and D.A. Moreno, *Int. J. Mol. Sci.*, **21**, 1998 (2020); https://doi.org/10.3390/ijms21061998
3. T.O. Ajiboye, T.T. Ajiboye, R. Marzouki and D.C. Onwudiwe, *Int. J. Mol. Sci.*, **23**, 1317 (2022); https://doi.org/10.3390/ijms23031317
4. G. Hogarth, *Mini-Rev. Med. Chem.*, **12**, 1202 (2012); https://doi.org/10.2174/138955712802762095
5. R. Cea-Olivares, R.A. Toscano, C. Silvestru, P. Garcia-Garcia, M. Lopez-Cardoso, G. Blass-Amador and H. Noth, *J. Organomet. Chem.*, **493**, 61 (1995); https://doi.org/10.1016/0022-328X(95)05342-M
6. M. Styblo and D.J. Thomas, *Biochem. Pharmacol.*, **49**, 971 (1995); https://doi.org/10.1016/0006-2952(95)00008-N
7. M. Stoytcheva, V. Sharkova and M. Panayotova, *Anal. Chim. Acta*, **364**, 195 (1998); https://doi.org/10.1016/S0003-2670(98)00134-2
8. R.A. Zakharyan and H.V. Aposhian, *Chem. Res. Toxicol.*, **12**, 1278 (1999); https://doi.org/10.1021/tx9901231
9. S.S. Garje, V.K. Jain and E.R.T. Tiekink, *J. Organomet. Chem.*, **538**, 129 (1997); https://doi.org/10.1016/S0022-328X(96)06905-7
10. A.A. Aly, A.B. Brown, T.M.I. Bedair and E.A. Ishak, *J. Sulphur Chem.*, **33**, 605 (2012); https://doi.org/10.1080/17415993.2012.718349
11. M.S. Kang, E.K. Choi, D.H. Choi, S.-Y. Ryu, H.-H. Lee, H.-C. Kang, J.-T. Koh, O.-S. Kim, Y.-C. Hwang, S.-J. Yoon, S.-M. Kim, K.-H. Yang and I.-C. Kang, *FEMS Microbiol. Lett.*, **280**, 250 (2008); https://doi.org/10.1111/j.1574-6968.2008.01069.x
12. H. Nabipour, S. Ghammamy, S. Ashuri and Z.S. Aghbolagh, *Org. Chem. J.*, **2**, 75 (2010).
13. R. Ghorbani-Vaghei, M. Amiri and H. Veisi, *Bull. Korean Chem. Soc.*, **33**, 4047 (2012); https://doi.org/10.5012/bkcs.2012.33.12.4047
14. N. Manav, A.K. Mishra and N.K. Kaushik, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **65**, 32 (2006); https://doi.org/10.1016/j.saa.2005.09.023
15. N.F. Kamaludin, N. Awang, I. Baba, A. Hamid and C.K. Meng, *Pak. J. Biol. Sci.*, **16**, 12 (2012); https://doi.org/10.3923/pjbs.2013.12.21
16. S.Z. Khan, M.K. Amir, I. Ullah, A. Aamir, J.M. Pezzuto, T. Kondratyuk, F. Bélanger-Gariepy, A. Ali, S. Khan and Zia-ur-Rehman, *Appl. Organomet. Chem.*, **30**, 392 (2016); https://doi.org/10.1002/aoc.3445
17. A.S. Sonia and R. Bhaskaran, *J. Mol. Struct.*, **1134**, 416 (2017); https://doi.org/10.1016/j.molstruc.2016.12.097
18. C.I. Yeo, E.R.T. Tiekink and J. Chew, *Inorganics*, **9**, 48 (2021); https://doi.org/10.3390/inorganics9060048
19. B.N. Saglik, Y. Özkay, Ü.D. Özkay and H.K. Gençer, *J. Chem.*, **2014**, 387309 (2014); https://doi.org/10.1155/2014/387309
20. S. Tamilvanan, G. Gurumoorthy, S. Thirumaran and S. Ciattini, *Polyhedron*, **121**, 70 (2017); https://doi.org/10.1016/j.poly.2016.09.038
21. S. Tamilvanan, *Asian J. Chem.*, **34**, 42 (2021); https://doi.org/10.14233/ajchem.2022.23409
22. M. Alam and S. Park, *J. Mol. Struct.*, **1159**, 33 (2018); https://doi.org/10.1016/j.molstruc.2018.01.043
23. S. Tamilvanan, G. Gurumoorthy, S. Thirumaran and S. Ciattini, *Polyhedron*, **123**, 111 (2017); https://doi.org/10.1016/j.poly.2016.10.026
24. H.L.M. Van Gaal, J.W. Diesveld, F.W. Pijpers and J.G.M. Van der Linden, *Inorg. Chem.*, **18**, 3251 (1979); https://doi.org/10.1021/ic50201a062
25. T.A. Koopmans, *Physica*, **1**, 104 (1934); https://doi.org/10.1016/S0031-8914(34)90011-2