SYNTHESIS, CHARACTERIZATION, BIOLOGICAL EVALUATION, AND DFT STUDIES OF As(III) DITHIOCARBAMATE COMPLEX

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Abstract

Elements analysis, NMR spectroscopy, and FT-IR spectroscopy were used to successfully synthesise and characterise a new As(III)-dithiocarbamate complex. The CN band obtained at 1470 cm^{-1} for the complex indicates its partial double-bonded nature. By using the GIAO technique, ^{13}C NMR and ^{1}H NMR analyses were performed with the DFT/B3LYP method with a LANL2DZ base set. Chemical reactivity of the molecule, MEP surface, HOMO-LUMO analysis, and dipole moment are illustrations of molecular characteristics that have been studied at the same level of theory. Thioureide (CN) and CS bands are experimentally noticed at 1459 and 1011 cm^{-1}, which were determined computationally to be 1467.82 cm^{-1} and 922.13 cm^{-1}, respectively, using the DFT (B3LYP/LANL2DZ) method. The molecular structure contains C-N and C-S bond distances which ranged between 1.3525 to 1.3599 Å and 1.7377 to 1.8428 Å, respectively. The use of the Agar-well diffusion method, the complex's antibacterial activity was investigated against bacteria, and fungus species.

Keywords: Arsenic, HOMO, LUMO, DFT, Dithiocarbamate, Antimicrobial.

INTRODUCTION

Main group (As(III), Sb(III) & Bi(III)) dithiocarbamate complexes have various applications in organic synthesis[1], analytical chelating agents [2], radiation protectors [3], antioxidants [4] and materials, and they have the potential to be used as pesticides, fungicides, and chemotherapeutics. Furthermore, dithiocarbamate derivatives are also used as anthelmintic [5], herbicidal [6], antiradiation agents [7], antioxidant [8], antiparkinson [9], and growth depressant [10]. The research on main group dithiocarbamates has not had a thorough examination since the 1970s [11, 12]. Numerous studies have been performed on [As(S2CNR2)3] homoleptic tris(dithiocarbamate) complexes. Dithiocarbamate complexes with arsenic, antimony, and bismuth in addition to other 1,1-dithiolate contain previously been reviewed [13]. The three small As-S bond lengths (As–S, 2.31 – 2.39 A˚) that are basically cis to each other and the 3 long As-S bond distances (As–S, 2.77 – 2.94 A˚) are also what make the arsenic dithiocarbamate complexes mononuclear. The pyrrolidine dithiocarbamate complex [$As(C_6H_4)_2O\ S_2CN(CH_2)_4$]. The x-ray molecular structure reveals that the dithiocarbamate is highly anisobidentate [As–S(long) (3.18 A; As–S(short) (2.28)].

The bonding between the metal centre and the nonbridging dithiocarbamate ligands is significantly less asymmetric than that of the comparable arsenic dithiocarbamate complexes. Calculations of the valency of bonds show that the valency of the arsenic atom's is near three, which is to be predicted [14]. The stereo chemically energetic lone pair along with a pseudo axis caps the triad face created by the three weakly coordinated sulphur atoms in the arsenic dithiocarbamate [$As(S_2CNR_2)_3$], resulting in a distorted octahedron [15, 16]. While the results are incongruent with a basic 1:1 electrolyte, conductimetry size of the As(III)diiodide of the complex [$AsI_2Me(S_2CNMe_2)$] generated by combining tetramethyl-thiuram disulfide with AsI_2Me reveal that it is ionic in solution [17]. The arsenic atom has a highly distorted trigonal-bipyramidal, if both sulphur atoms are involved in the arsenic atom of the complex. The main group dithiocarbamates complexes [ML_3XY], and [ML_2XY_2] have been studied for their antimicrobial potential.

EXPERIMENTAL

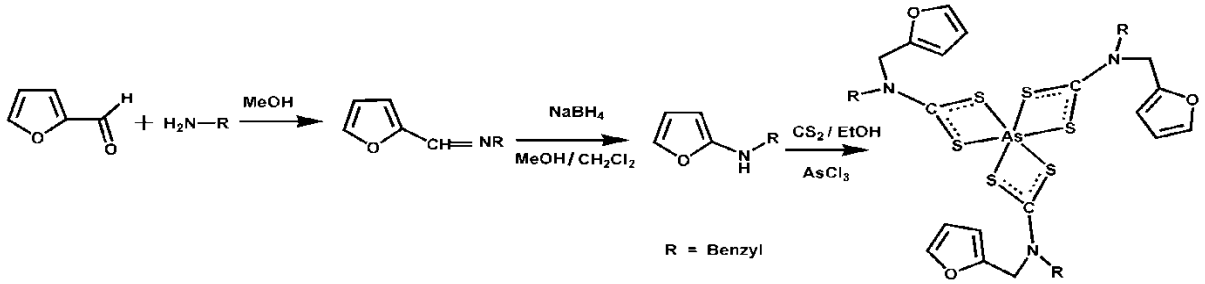
General procedure

Preparation of amine:

N-furfuryl-N-benzylamine was prepared with furfuraldehyde, benzylamine, and sodium borohydride ($NaBH_4$). Methanol was utilized to dissolve the amine and aldehyde, and the mixture was agitated for three hours at RT. At 5°C, sodium borohydride was added to this solution of mixture, which was agitated for 12 hours at RT to get N-furfuryl-N-benzylamine [18].

Synthesis of the metal dithiocarbamate complex:

Under ice-cold (5°C) conditions, amine and CS_2 were added in C_2H_5OH and swirled for 30 minutes. Arsenic trichloride was then gently added to the mixture while it was being stirred continuously. The resulting product crystallized. Scheme-1. Yield: (79%), mp. 179°C. Anal. Calc. for $C_{39}H_{36}N_3O_3S_6As$ (862.03): C, 54.34; H, 4.21; N, 4.87 Found : C, 54.28; H, 4.16; N, 4.81%. IR: Experimental: 1459 cm^{-1} (CN), 1011 cm^{-1} (CS), 2872 cm^{-1} (CH), Theoretical: 1467.82 cm^{-1} (CN), 922.13 cm^{-1} (CS), 3080.94 cm^{-1} (CH), ^1H NMR (400 MHz, $CDCL_3$, ppm): Experiment: 5.02 (N-CH_2-C_6H_5); 5.21 (methylene furyl) ; 6.29-7.34; Theoretical: 2.8363 (75H) (N-CH_2-C_6H_5); 4.7524 (66H) (methylene furyl); (69H - 5.5599) (71H - 5.8917) (87H - 6.5600) (81H - 7.0201) (83H - 7.0201) (85H - 7.0201) (73H- 7.2021) (79H - 7.2021): ^{13}C NMR ($CDCL_3$, ppm); Experiment : 48.1 (CH_2-C6H_5); 55.1 (methylene furyl), 142.5, 110.6, 148.6 , 110.4, (furyl ring carbons); 128.1, 128.0, 134.1, 128.2, (phenyl ring carbons) 203.3 (NCS_2):: Theoretical: 52.5924 (74C) (CH_2-C_6H_5); 44.6555 (64C) (CH_2 furfuryl), (70C - 102.8126), (68C - 105.3419), (72C - 142.2676) (67C - 150.7731) (furyl carbons); (78C - 122.1358) (77C - 129.4966) (80C - 123.2529) (82C - 120.3287) (84C - 121.7974) (86C - 122.6860) (phenyl ring carbons) 234.3328 (63C) (NCS_2):



Scheme 1. Synthesis of the metal complex

Computational details:

Quantum chemical computations were examined by using the B3LYP/LANL2DZ basis set via Gaussian 9W [19] software for the dithiocarbamate complex. In the gas phase, the complex's molecular geometry optimization and vibrational frequencies were computed. The GIAO [20] techniques were used to generate the ^1H and ^{13}C NMR spectra at DFT.. Electronic properties such as FMOs HOMO, LUMO, Molecular electrostatic potential surface and contour maps, Mulliken atomic charges are computed by DFT with a LANL2DZ base set.

Antimicrobial studies:

Antimicrobial activities were investigated using the Mueller-Hinton disc diffusion technique [21]. To prepare the petri plates, 20 mL of Mueller-Hinton agar was added. To create discs with various concentrations of the tested compound (required concentrations - 400 and 800 µg), sterile blank discs

were saturated with 15 L of the stock solution's known content. The reference drug was Ciprofloxacin. For bacteria and fungi, the plates were incubated for 24 hours at 37ºC and 27ºC, respectively. Zones of inhibition were recorded in millimetres. The bacterial and fungal strains were *V. cholerae, K. pneumoniae, S. aureus, E. coli, C. albicans and A. niger.*

RESULTS AND DISCUSSION

Infrared and NMR analysis

The C-S and C-N stretching vibration modes, which typically lie within the ranges of 980 ± 50 and 1500 ± 50 cm^{-1}, respectively, have been specifically used analytically in the FT-IR spectrum of the dithiocarbamate complex [22]. Thioureide (C-N) and C-S wave numbers are noticed at 1459 cm^{-1} and 1011, which were computed as 1467.82 cm^{-1} and 922.13, respectively, by the DFT/LANL2DZ technique.

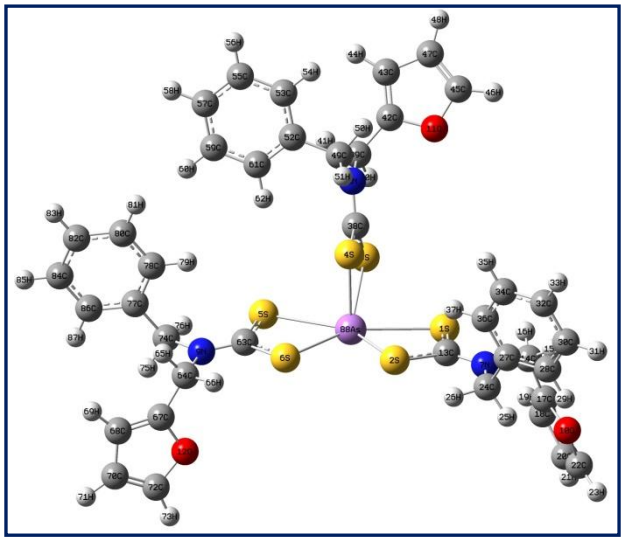
The DFT-B3LYP/LANL2DZ method was used for complex molecule optimization. The ^{1}H NMR and ^{13}C NMR spectra were done by the GIAO method. The ^{1}H NMR and ^{13}C NMR chemical shifts were performed in $CDCL_3$ using tetramethylsilane as an reference. The theoretical and experimental values of ^{1}H NMR and ^{13}C NMR were recorded. Experimentally, two singlets are detected in the complex's proton NMR spectra in the 5.02–5.21 ppm range, whereas the predicted range is 2.8363–4.7524 ppm. Experimental and theoretical analyses show that the aromatic ring protons are at 6.29–7.34 ppm and 5.55–7.2021 ppm, respectively. Two signals are found in the complex's 13C NMR spectra experimentally at 48.1 ppm and 55.1 ppm, respectively, due to the CH2 carbons of aromatic ring , although the theoretical range is 44.6555-52.5924 ppm. The $N^{13}CS2$ weak intensity carbon signal was measured experimentally at 203.3 ppm and theoretically at 234.3328 ppm.

Molecular geometry*:*

The DFT/B3LYP procedure with a LANL2DZ base set through Gaussian 9W [45-50] was used to get the investigation's optimum geometry, which is depicted in Figure 1. The arsenic(III) dithiocarbamate complex has an energy of -1964.1273 eV and a dipole moment of 4.341 eV, respectively. The bond lengths, bond angles, and dihedral angles of the compound were computed. . The molecular structure contains C-N and C-S bond distances which ranged between 1.3525 to 1.3599 Å and 1.7377 to 1.8428Å, correspondingly. The bond angle (66.6322° (S5-As88-S6)) and dihedral angle (178.3382° (As88-S1-C13-N7)) of the As(III) complex are determined. The CS bond lengths (mean: 1.7892), which are midway between double and single bond distances, indicate the existence of partial double bonds. Table 2 provides a list of the complex's molecular structural properties.

Table 1 Calculated energy values of the complex

Parameters of the molecule	Value
	eV
HOMO value	-5.7266
LUMO value	-1.9592
Energy Gap value	3.7674
(IP)	5.7266
(EA)	1.9592
(η)	1.8837
(μ)	-3.8429
(χ)	3.8429
(S)	0.2654
(ω)	3.9199



Energy	-1964.1273
Dipole Moment	4.3410

Fig. 1 Optimized structure of the complex

Frontier molecular orbital's analysis:

Frontier molecular orbitals of the complex can provide information regarding photochemical reactions, pharmaceutical studies, electrical characteristics, and optical characteristics. The energy values of both the HOMO and LUMO are highly helpful for determining chemical reactivity like electrophilicity (ω), global hardness (η), and other parameters are computed at DFT and given in Table 1. The orbital energies and the energy gap of the arsenic dithiocarbamate complex are computed using the B3LYP/DFT method with a LANL2DZ base set. HOMO is mostly located on the rings and sulphur atom, while LUMO is mostly located on the arsenic, carbon, and nitrogen atoms of the complex.

The ionisation energy and the electron affinity are expressed in terms of IP = $-E_{HOMO}$ (5.7266 eV) and EA = $-E_{LUMO}$ (1.9592 eV), respectively, according to Koopman's theorem [23]. Using frontier molecular orbital parameters, Mulliken electronegativity is calculated as = - ½ (E_{HOMO} + E_{LUMO}) (3.8429 ev). If the substance has a high electronegativity value, the molecule or element will attract electrons to itself. The formula for calculating the global softness is as follows: S = 1/ 2η (0.2654 eV) denotes a molecule's ability to receive electrons. The global hardness (η) can be computed as η = ½ (E_{LUMO} - E_{HOMO}) (1.8837 eV), which measures an atom's resistance to charge transfer. For analysing the chemical reactivity of molecules, electrophilicity is a helpful structural characterisation of reactivity that is often used. Its index is written as $\omega = \mu^2/2\eta$ = 3.9199 eV, which *Parr et al* [24]. described. The electrophilicity index (ω) = 3.9199 eV, global softness (S) = 0.2654 eV, the chemical hardness (η) =1.8837 eV and the electronegativity (χ)= 3.8429 eV for the As(III) complex at the B3LYP/LANL2DZ basis set. The energy connection between HOMO and LUMO is shown in Table.1, and Figure 2 depicts the figure.

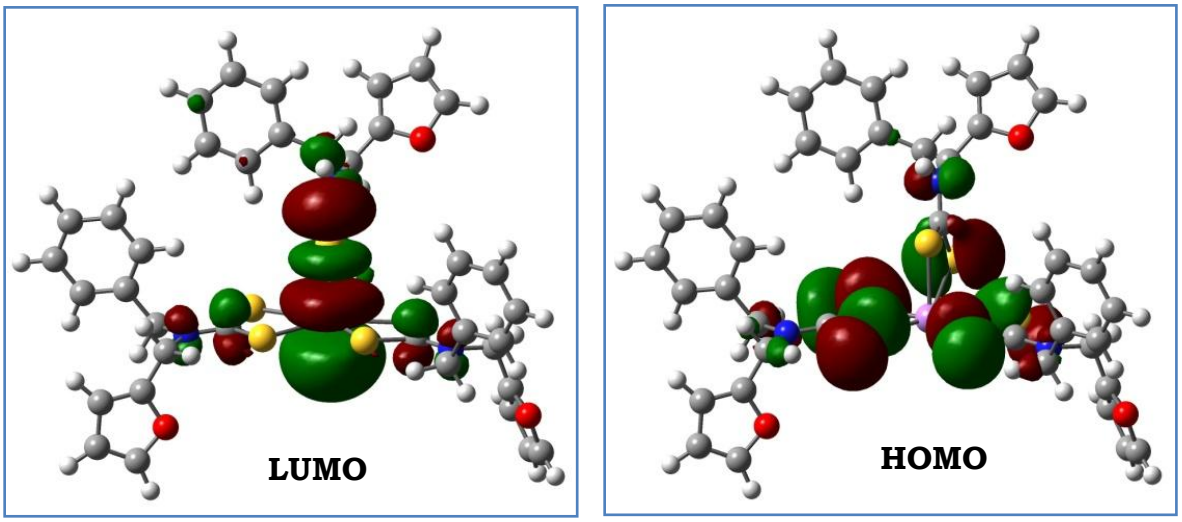


Fig. 2 HOMO - LUMO plots of the geometry molecule.

Table. 2 bond distances (Å), bond angles and dihedral angles (°) chosen for the complex

Bond Distances (Å)		Bond Angles (°)		Dihedral Angles (°)	
S1-C13	1.7665	C13-S1-As88	84.2475	As88-S1-C13-S2	-2.5109
S1-As88	2.8718	C13-S2-As88	90.5498	As88-S1-C13-N7	178.3382
S2-C13	1.8126	C38-S3-As88	78.4237	C13-S1-As88-S2	1.6521
S2-As88	2.6407	C38-S4-As88	95.5387	C13-S1-As88-S3	157.4181
S3-C38	1.7377	C63-S5-As88	84.1457	C13-S1-As88-S4	92.2645
S3-As88	3.0623	C63-S6-As88	91.2903	C13-S1-As88-S5	173.1501
S4-C38	1.8428	C13-N7-C14	121.4992	C13-S1-As88-S6	-9.791
S4-As88	2.4484	C13-N7-C24	123.8869	As88-S2-C13-S1	2.7171
S5-C63	1.7689	C14-N7-C24	114.5798	As88-S2-C13-N7	178.1015
S5-As88	2.9054	C38-N8-C39	120.9147	C13-S2-As88-S1	-1.6021
S6-C63	1.8066	C38-N8-C49	123.8794	C13-S2-As88-S3	-36.8825
S6-As88	2.6538	S1-As88-S2	67.3829	C13-S2-As88-S4	-94.736
N7-C13	1.3525	S1-As88-S3	76.0407	C13-S2-As88-S5	173.4742
N7-C14	1.495	S1-As88-S4	93.6485	C13-S2-As88-S6	171.7849
N7-C24	1.4953	S1-As88-S5	147.2408	As88-S3-C38-S4	4.7365
N8-C38	1.3599	S1-As88-S6	145.3246	As88-S3-C38-N8	175.0607
N8-C39	1.4941	S2-As88-S3	136.3956	C38-S3-C38-S1	103.5915
N8-C49	1.4865	S2-As88-S4	91.9667	C38-S3-As88-S2	-70.2667
N9-C63	1.3581	S2-As88-S5	145.1697	C38-S3-As88-S4	-3.3933
N9-C64	1.493	S2-As88-S6	78.5527	C38-S3-As88-S5	92.3673
N9-C74	1.4878	S3-As88-S4	66.9459	C38-S3-As88-S6	65.6717
O10-C17	1.4112	S3-As88-S5	75.2565	As88-S4-As88-S3	-5.8342
O10-C22	1.3991	S3-As88-S6	137.4604	As88-S4-As88-N8	173.9799
O11-C42	1.4034	S4-As88-S5	89.4074	As88-S1-C13-S2	-2.5109
O11-C45	1.3968	S4-As88-S6	93.7988	As88-S1-C13-N7	178.3382
O12-C67	1.4028	S5-As88-S6	66.6322	C13-S1-As88-S2	1.6521

Molecular electrostatic potentialb(MEP):

The charge distribution of a molecule is shown by MEP energy. The electron-rich region of the molecular geometry is indicated by the colour red, and the electron-poor region is indicated by the colour blue. The MEP's structure is further supported by the information that it continually display molecule dimension, shape, and neutral, positive, and negative colour grade region. This large electronegativity gap produces regions that are almost totally red and blue. These maps are color-coded in the compound variety between -4.706 e^{-2} and +4.706 e^{-2}. The location of the methyl and amino groups indicates a region that may resist nucleophilic attacks since it is particularly positive. There were no positive or negative potential atoms in the depletion region. The electrostatic potential increases sequentially from

red < orange < yellow < green < blue. Further, it provides a graphical representation of the intrinsic polarity of the molecule. Figure 3 depicts the surface's contour map, which was created using the same grade of calculation as the complex.

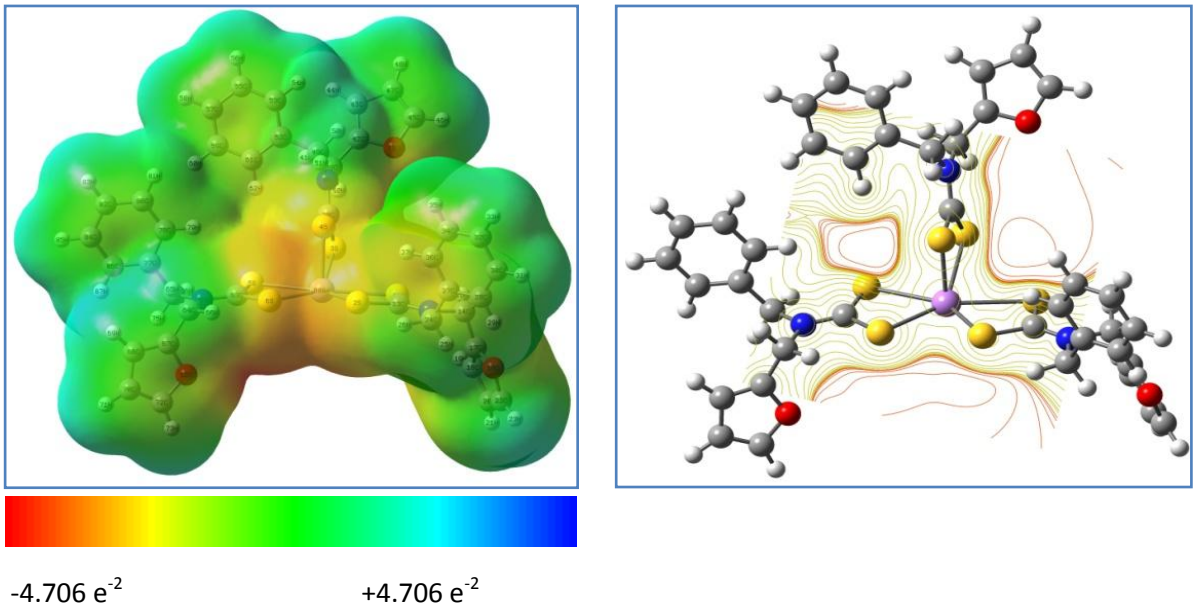


Fig. 3 MEP surface (left) and contour map (right) of the complex.

Mulliken charges analysis:

The Mulliken atomic charges [25] for the complex were determined using the DFT/B3LYP method with a LANL2DZ base set. Table 3 lists the atomic charges for each individual atom of the complex. A Mulliken atomic charge calculation is required for the use of quantum chemical analysis of molecule structure. All hydrogen (H) atoms in the complex exhibited a net positive charge, but H15 = 0.2765 gained the most positive charge compared to the other hydrogen atoms because electronegative atoms were present. On carbon (C) atoms, the value of the Mulliken atomic charge might be positive or negative. A few carbon atoms are most positively charged: C13 (0.4938), C14 (0.4930), and C17 (0.4869). Mulliken's atomic charge analysis of the complex is exposed in Fig. 4.

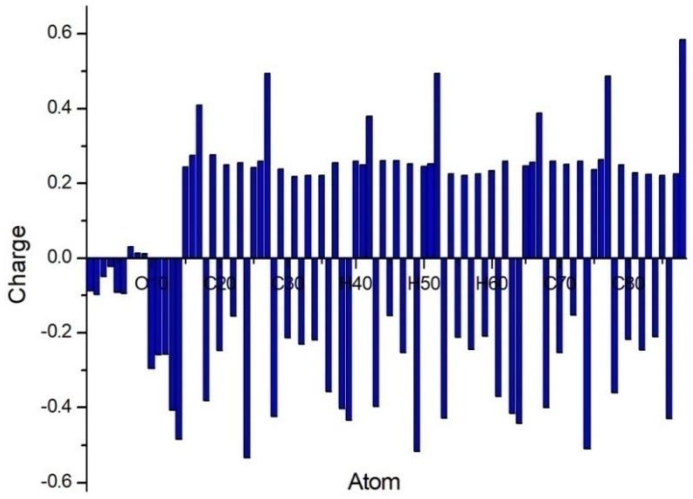


Fig. 4 The complex's Mulliken atomic charge analysis

Table. 3 Mulliken method of charge distribution

atoms	charges	atoms	charges	atoms	charges	atoms	charges
S1	-0.08613	H23	0.255267	C45	-0.15313	C67	0.389054
S2	-0.09698	C24	-0.5325	H46	0.261134	C68	-0.40002
S3	-0.04919	H25	0.243278	C47	-0.25246	H69	0.260113
S4	-0.02099	H26	0.260039	H48	0.252422	C70	-0.25239
S5	-0.09153	C27	0.493097	C49	-0.51575	H71	0.251531
S6	-0.09355	C28	-0.42402	H50	0.245467	C72	-0.15196
N7	0.030683	H29	0.238216	H51	0.252557	H73	0.260426
N8	0.013443	C30	-0.21335	C52	0.493874	C74	-0.50766
N9	0.012276	H31	0.219782	C53	-0.42742	H75	0.236641
O10	-0.29485	C32	-0.2298	H54	0.225395	H76	0.263767
O11	-0.25795	H33	0.222392	C55	-0.21176	C77	0.486903
O12	-0.25655	C34	-0.21808	H56	0.222343	C78	-0.36002
C13	-0.40691	H35	0.221298	C57	-0.24414	H79	0.25036
C14	-0.48345	C36	-0.35714	H58	0.226321	C80	-0.21706
H15	0.244142	H37	0.256515	C59	-0.20796	H81	0.228915
H16	0.275002	C38	-0.40149	H60	0.234904	C82	-0.24523
C17	0.410055	C39	-0.43389	C61	-0.36943	H83	0.224825
C18	-0.38103	H40	0.259967	H62	0.26043	C84	-0.21005
H19	0.276509	H41	0.249759	C63	-0.41491	H85	0.221928
C20	-0.24629	C42	0.379749	C64	-0.44224	C86	-0.42882
H21	0.250792	C43	-0.39615	H65	0.246966	H87	0.226309
C22	-0.15449	H44	0.261705	H66	0.257647	As88	0.584506

Measurement of antimicrobial activity:

Through a disc diffusion technique at 400 and 800 µg/disc concentrations. The As(III) dithiocarbamate complex was tested using four bacteria: *K. pneumoniae, S. aureus, E. coli and V. cholerae*. Two other fungi were also chosen, *C. albicans* and *A. niger*. The antimicrobial activity of the complex was compared to that of ciprofloxacin. Table 4 provides a summary of the results and a description of the antimicrobial action (inhibition zone). According to antimicrobial investigations, the complex revealed medium activity against both of the tested fungus species when compared to the

standard drug (Ciprofloxacin). A histogram of the complex's antimicrobial activity is shown in Figure 5. The As(III) complex studies revealed lower antibacterial action contrary to *K. pneumoniae* in addition to increased antifungal action contrary to *A. nigeria*.

Table. 4 The complex's antimicrobial properties

Complex	**Disc Plate**	**bacteria**				**fungal**	
	(µg)	***V. cholera***	***S. aureus***	***K. pneumoniae***	***E. coli***	***C. albicans***	***A. Niger***
	400	8	7	4	6	4	7
	800	14	12	10	12	8	15
Ciprofloxacin		35	26	34	35	35	26

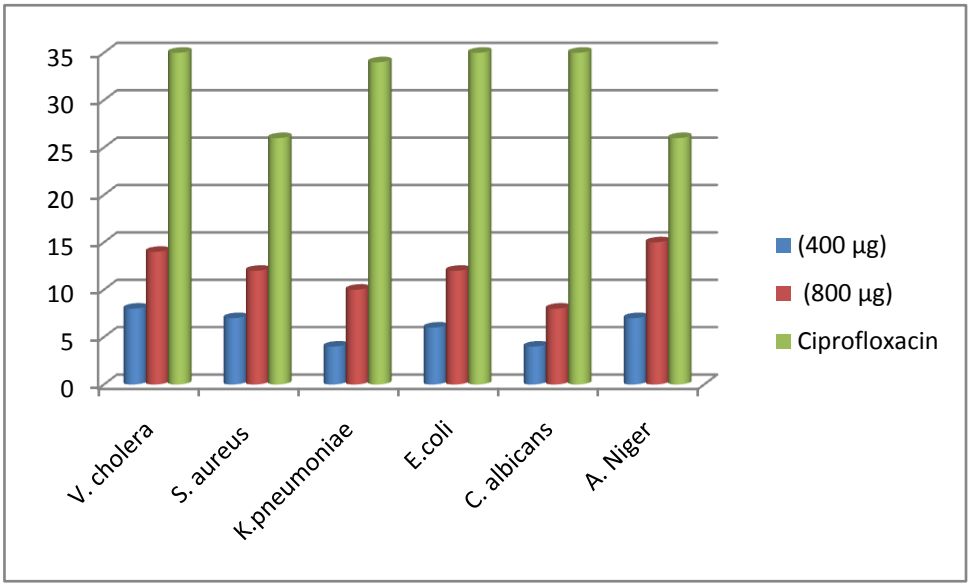


Fig. 5 Histogram representation of antimicrobial activity

CONCLUSION

In this work, we have synthesized a novel As(III) dithiocarbamate complex by a superior way. In order to determine the geometric structure, HOMO-LUMO, MEP, and Mulliken atomic analyses as well as the spectral analyses containing the IR and NMR were performed using the same level in the gas phase at the B3LYP method with a LANL2DZ base set. The complex's molecular structure has C-N and C-S bond lengths that range from 1.3525 to 1.3599 Å and 1.7377 to 1.8428 Å, respectively. The electrophilicity index (ω) = 3.9199 eV, global softness (S) = 0.2654 eV, the chemical hardness (η) =1.8837 eV and the electronegativity (χ)= 3.8429 eV for the As(III) complex at the B3LYP-LANL2DZ

base set. All hydrogen (H) atoms in the complex exhibited positive charges, where H15 = 0.2765 gained the most positive charge compared to the other hydrogen atoms because electronegative atoms were present. The title complex's antimicrobial activities were in the order of *C.albicans* < *K.pneumonia* < *E.coli* < *S.aureus* < *V.cholera* < *A. Niger.*

CONFLICT OF INTEREST

Dr.S.Tamilvanan and co-authors declare that they have no conflicts of interest

AUTHOR CONTRIBUTION

Dr.S.Tamilvanan and Dr.G.Manikandan contributed to the preparation and execution of the research, analysis of the data, and manuscript writing.

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