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Synthesis and physicochemical studies on 4-methylpiperazine-1-carbodithioic acid capped silver nanoparticles

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ABSTRACT

Stable silver nanoparticles were synthesized with a passivating monolayer of 4-methylpiperazine-1-carbodithioic acid (4-MPipzcdtH) - derivative of heterocyclic amine, 1-methylpiperazine (1-MPipz). Particles were characterized by elemental analysis and energy dispersive analysis of X-rays (EDAX). SEM images of powdered sample revealed spherical shape. Core diameter of resulting nanoparticles was determined to lie in 3-5 nm range using transmission electron microscopy (TEM). ^{1}H NMR and IR spectroscopy studies were used to check the particle purity. XRD patterns indicated arrangement of silver nanoparticles with a face centered cubic (fcc) structure. Surface plasmon resonance peak has been observed at 430 nm. Paramagnetic nature of particles (μ_{eff}=1.74 B.M.) supports reduction of silver (I) to silver (0). Lipase activity assay of capped silver nanoparticles with different core diameters exhibited reduction in activity with decreasing metal feed ratio. Silver (I) complex of 4-MPipzcdtH has also been synthesized and investigated. The results have been compared with those of 4-MPipzcdtH capped Ag nanoparticles.

KEYWORDS

Silver;
Nanoparticles;
Capping agent;
4-methylpiperazine-1-carbodithioic acid;
TEM;
Spectra;
Lipase activity.

INTRODUCTION

A rich variety of methods to prepare silver nanoparticles exist. But due to highly exposed surface, the nanoparticles tend to aggregate and form large clusters even during the preparation process. As a result it is critical to control the particle-particle interactions so as to obtain stable dispersions. Silver is reactive to sulphur, in particular bulk silver often undergoes to tanning due to formation of Ag_2S sulphur layer. Therefore, in case of sulphur containing molecules, ligation to nanoparticles surface is particularly effective for the contemporary presence of a σ type bond, in which sulphur is electron density donor and metal atom is acceptor, plus a π type bond in which metal electrons are particularly delocalized in a molecular orbital formed between the filled d-orbitals of metal and empty d-orbitals of sulphur[1]. Although, sulphur containing thiols based ligands act as versatile capping agents, but they can be displaced from metal surface[2], incompatible with other functional group associated with the ligand and to improve the dimension and properties of nanoparticles. Dithiocarbamates based capping agents/ligands have gained substantial attention as the robust motifs to construct functional nanostructures.

Dithiocarbamates are versatile ligands with a wide range of chemistry. The applications of dithiocarbamate ligands have been demonstrated in the construction of new supramolecular motifs such as polymetallic nanosized macrocrystals[3]. Molecules containing dithiocarbamate group construct the functional nanostructure by exchanging the original ligands of metal. Characteristics for dithiocarbamates are the presence of nitrogen in the anchor group and the capability to bind symmetrically with both sulphur atoms to metal surface, where metal is in zero oxidation state. Dithiocarbamates are also capable of stabilizing transition metals in a variety of oxidation states, for silver +1 is the most stable oxidation state. Stabilization of particular oxidation state is due to charge levelling by σ and π back bonding. Nanomaterials also display potential antibacterial applications, like silver nanoparticles can be incorporated in wound dressing, footwear, paints and plastic for their antibacterial property[4,5]. Silver nanoparticles are also used in biosensors[6] and numerous assays where the nanoparticle materials are used as biological tags for quantitative detection[6].

MATERIAL AND METHODS

Chemicals

Ethanol (99.5%, Bengal chemicals), carbon disulphide, toluene, silver nitrate and dimethyl sulphoxide (DMSO), all from Merck, AR were used as obtained. 1-Methylpiperazine (1-MPipz) (Fluka) was dried by refluxing over sodium hydroxide beads. The colourless liquid obtained after distillation was stored over sodium hydroxide beads in a vacuum desiccator for three days before use.

Preparation of Chemical Capping Agent/Ligand: 4-Methylpiperazine-1-carbodithioic acid (4-MPipzcdtH)

1-Methylpiperazine (0.66 g; 0.66 mmol) in ethanol (1.5 ml) was cooled to 5 ^{0}C. To this cooled solution carbon disulphide (0.05 g; 0.66 mmol) was added slowly with stirring when light yellow solid separated. The product was filtered and washed 2-3 times with ethanol. It was dried in $CaCl_2$ desiccator.

Preparation of 4-MPipzcdtH capped silver nanoparticles

A solution of ($AgNO_3$) (0.113 g; 0.66 mmol) in ethanol (2.62 ml) was prepared. To this solution toluene (26.2 ml) was added and the mixture was stirred for 1 minute. Suspension of 4-MPipzcdtH in ethanol (0.116 g;.66 mmol) was added to it while stirring which yielded a yellow colour. The mixture was stirred for another 5 minutes. Ethanolic solution of sodium borohydride ($NaBH_4$) (0.125 g; 3.3 mmol) was added to the above reaction mixture while stirring, when the solution turned dark black, stirred the mixture for another 5 minutes. Product was filtered and washed several times with ethanol using centrifugation technique. Black particles were dried in $CaCl\text{-}_2$ desiccator for overnight.

Three batches of 4-MPipzcdtH capped silver nanoparticles were prepared with the intial molar ratio of 4-MPipzcdtH to Ag as: 0.5:1, 1:1 and 1.5:1. The resulting particles were then denoted as (0.5×1), (1×1) and (1.5×1) respectively.

Preparation of [Ag(4-MPipzcdtH)](NO_3) complex

A solution of silver nitrate (0.113 g; 0.66 mmol) in ethanol (2.62 ml) was prepared. Suspension of 4-MPipzcdtH in ethanol (0.116 g;.66 m mol) was added to it while stirring which yielded a yellow colour and the mixture was stirred for another 5 minutes. The yellow coloured product was filtered and washed 2-3 times with ethanol using centrifugation technique. It was dried in $CaCl_2$ desiccator for overnight.

Elemental analyses and physical measurements

Silver and sulphur were determined gravimetrically as silver oxide and barium sulphate respectively. Carbon and hydrogen analyses were performed on an automatic Coleman-33 analyser while nitrogen was analysed by Kjeldahl's method. Scanning electron microscopy (SEM) measurements of silver nanoprticles (1×1) and complex of silver (I) were performed on quanta – 250, model no D9393 having magnification range 1-100000 X and maximum high voltage of 30 KV, connected to EDAX element quantification system. Transmission electron microscopy (TEM) measurements of silver nanoparticles (0.5×1) and (1.5×1) (powder sample dispersed in methanol fixed on a copper – supported carbon film) were performed on a

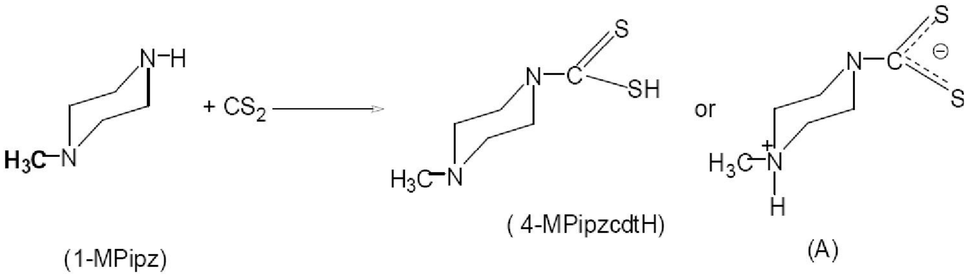
Hitachi microscope (H – 7500) 120 KV equipped with CCD camera. The instrument has resolution of 0.36 nm (point to point) with 40 – 120 KV opening voltage. Infrared spectra of ligand 4-MPipzcdtH, 4-MPipzcdtH capped silver nanoparticles and Ag (I) complex were recorded as KBr pellets on Nicolet 5700 FT Infrared Spectrophotometer in the 4000 – 600 cm^{-1} region. Infrared spectra of the compounds were also recorded as nujol mull with cesium chloride plates as windows in the 600 – 200 cm^{-1} region. ^{1}H NMR spectra of all these compounds were recorded on a BRUKER AVANCE II 400 NMR spectrometer using $(CD_3)_2SO$ as solvent. XRD patterns for different samples in powder form were taken in range of 10°– 80° with a step size of 0.050 (2 θ) with 1 sec counting time at each step using Cu – Kα (= 1.540) radiation source and a diffractometer system [XPERT–PRO]. Magnetic susceptibility measurements were performed on Vibrating Sample Magnetometer PAR-155 by varying the magnetic field from – 6000 to + 6000 Oe using $Cu(OOCCH_3)_2 . H_2O$ as calibrant. Electronic absorption spectra of compounds with solvent (DMSO) as the reference, were recorded on Bio Chem UV spectrophotometer (range 900 – 200 nm).

Biological studies

The activity of lipase enzyme (μmol/ml/min) in presence of compounds, i.e. 4-MPipzcdtH capped silver nanoparticles ((0.5×1), (1×1) and (1.5×1) compound) and $[(Ag(4\text{-}MPipzcdtH)](NO_3)$ was assayed by colorimetric method[7] using chromogenic p-nitrophenyl palmitate (pNPP) as substrate and subsequent measurement of absorbance of p-nitrophenol released (A_{410} nm). Different concentrations of test solution of compounds were used. Effect of incubation time for optimum concentration of the compounds has also been studied. An appropriate control (without addition of compound) was also used for each assay.

RESULTS AND DISCUSSION

The carbodithioate ligand (4-MPipzcdtH) of present investigation, used as capping agent for synthesis of silver nanoparticles, has been obtained from saturated heterocyclic secondary amine, i.e. 1-methylpiperazine (1-MPipz) by insertion of carbon disulphide as shown below:



Synthesis of silver nanoparticles in the presence of 4-MPipzcdtH as capping agent and $NaBH_4$ as reducing agent follows the reaction

$$AgNO_3 + n\,4\text{-MPipzcdtH} + NaBH_4 \xrightarrow[\text{toluene}]{\text{ethanol}} Ag\ n\,4\text{-MPipzcdtH} + NaNO_3 + \frac{1}{2}B_2H_6 + \frac{1}{2}H_2$$

n = 0.5, 1.0 or 1.5

Resulted silver nanoparticles are black, stable and fairly soluble in non-polar solvents (dichloromethane and DMSO).

4-MPipzcdtH complex of silver (I) was obtained according to the reaction

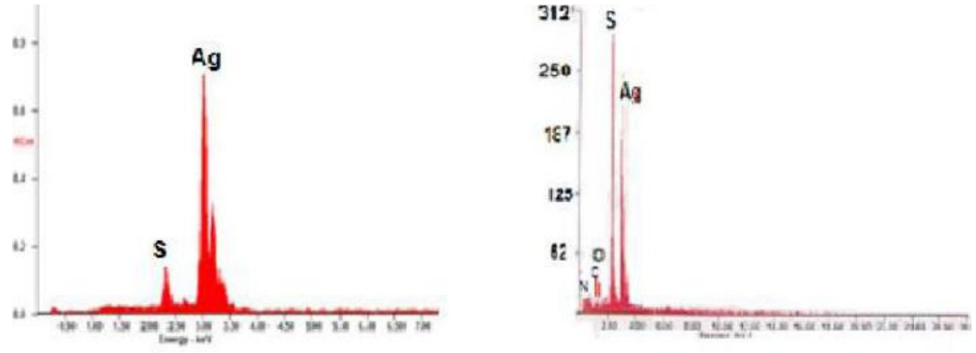
$$AgNO_3 + 4\text{-MPipzcdtH} \rightarrow [Ag\ (4\text{-MPipzcdtH})]\ (NO_3)$$

Silver (I) complex is fairly soluble in DMSO and water.

The 4-MPipzcdtH capped silver nanoparticles do not melt or decompose even at 350°C whereas, $[Ag(4\text{-}MPipzcdtH)](NO_3)$ does not melt but decomposes between 110 - 200°C. (TABLE 1)

EDAX

Chemical characterization using EDAX analysis of (1×1) sample revealed 93 wt% of silver in addition to 7 wt% of sulphur (Figure 1a). This provides evidence that sample contains silver and confirms the presence of capping agent around silver particles[8]. Whereas EDAX study of silver (I) complex ($[Ag\ (4\text{-}MPipzcdtH)]\ (NO_3)$) showed, silver 43 wt%, sulphur 17wt%, oxygen 15 wt%, nitrogen 11 wt% and carbon 14 wt% (Figure 1b). The data has further been complemented by elemental analysis (TABLE 1).



(a) (b)

Figure 1 : EDAX spectra of: (a) (Ag n4-MPipzcdtH) (1× 1) and (b) [Ag(4- MPipzcdtH)](NO3)

TABLE 1 : Elemental analytical data and physical data of 4-methylpiperazine -1-carbodithioic acid capped silver nanoparticles [Agn4-MPipzcdtH (1×1)] and Ag(I) complex

Sr. No	Compound	Elemental Analysis (Found); (EDAX); (Calc.) % C	H	N	S	Ag	Decomposition Temperature (^{0}C)	Colour
1	Ag n4-MPipzcdtH	- - -	- - -	- - -	(6.4) (7) -	(91.89) (93) -	stable	Black
2	Ag(4-MPipzcdtH)](NO$_3$)	(16); (14); (20.8)	(3.43); (2); (3.46)	(10); (11); (12.14)	(17.5); (17); (18.50)	(35); (43); (31.18)	110	Yellow

SEM

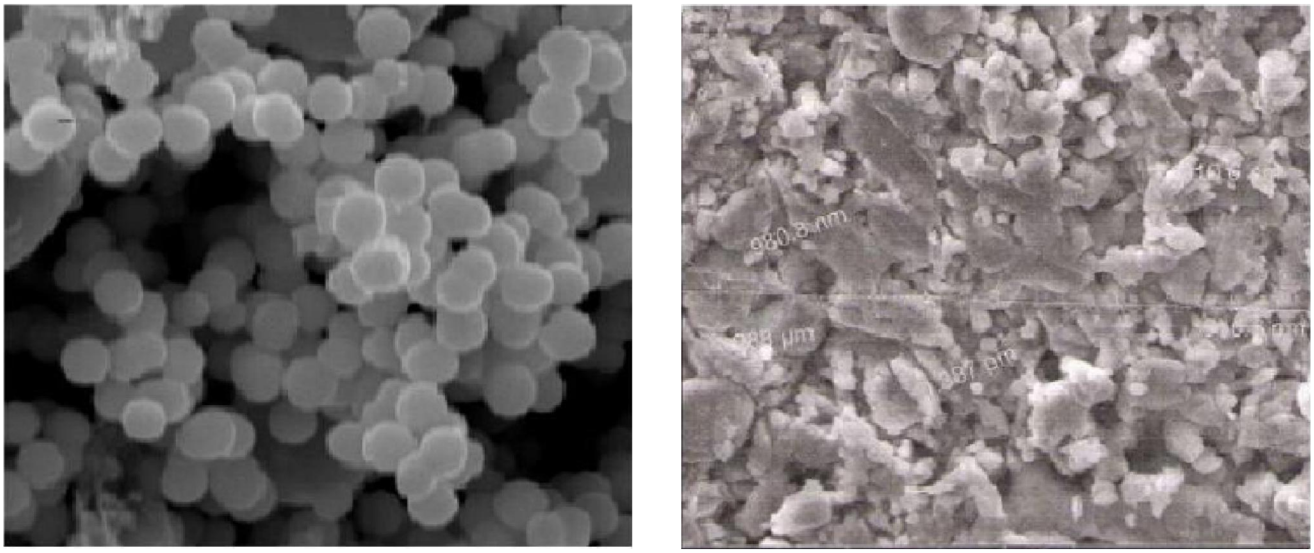
SEM micrograph of 4-MPipzcdtH capped silver (1×1) (Figure 2a) revealed that particles are spherical in shape with size 300-950 nm and possess regular arrangements but lack uniformity. The fact that particles are spherical in shape reveals that 4-MPipzcdtH is acting as capping agent thus leading to the formation of particles with definite shape. SEM image of Ag (I) complex ([Ag(4-MPipzcdtH)]NO$_3$) (Figure 2b) showed that there is no uniformity in size (980 nm – 400 μm) and shape of particles.

TEM

From the TEM study it can be seen that 4-MPipzcdtH-capped-Ag [(0.5×1) and (1.5×1)] nanoparticles particles exhibit spherical shapes with majority of particles falling in the range 3-5 nm in diameter (Figure 3). The particles are well monodispersed without any aggregation. This implies that 4-MPipzcdtH ligand has been strongly chemisorbed onto the silver surface and thus provides a very efficient passivating layer on the nanoparticles surface. The average core diameter of (0.5×1) and (1.5×1) samples is 4 and 3 nm respectively, which shows that average core diameter decreases with increasing initial ligand to metal feed ratio. This behavior resembles the DTC capped Ag[9] and Au[10] nanoparticles. Present investigation shows that dithiocarbamate derivative of hetrocyclic amine too provides better passivation.

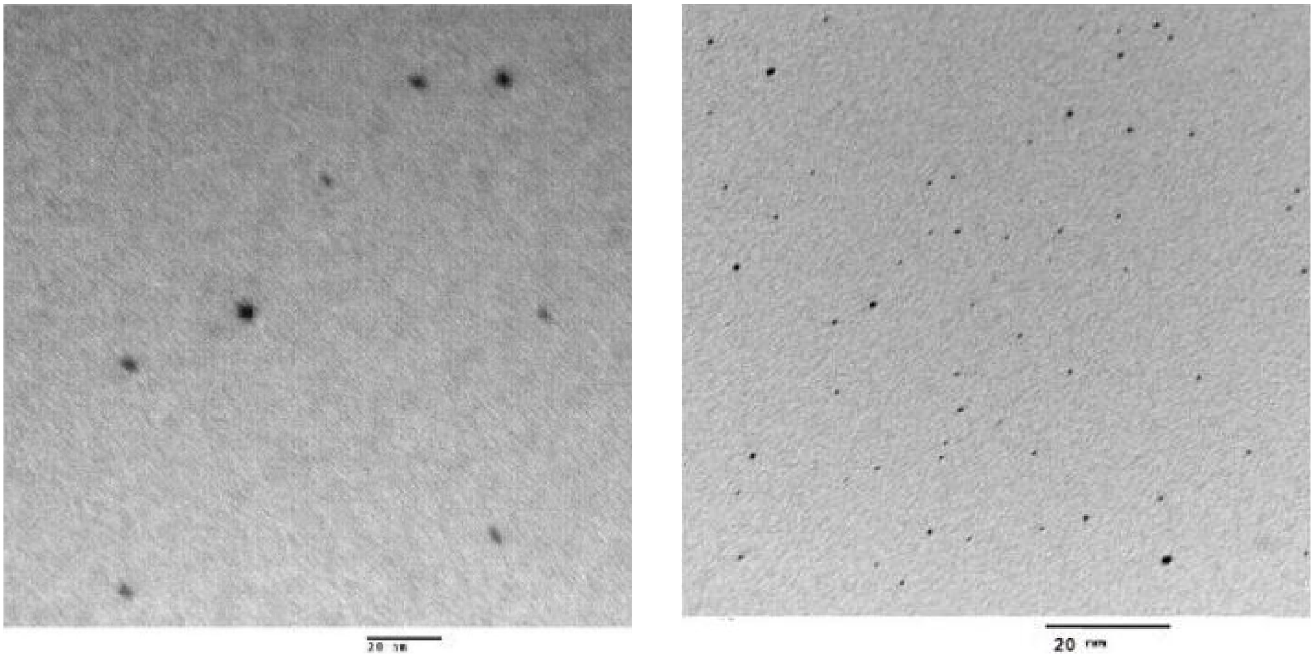
IR studies

In the free 4-methylpiperazine-1-carbodithioic acid, 4-MPipzcdtH capped Ag nanoparticles and complex [Ag(4-MPipzcdtH)](NO$_3$) a new broad band around 3600-3200 cm^{-1}, 3446-3427 cm^{-1} and 3428 cm^{-1} respectively has been observed. The appearance of this band points to formation of N%H bond supporting the presence of the carbodithioate ligand as a Zwitterion and this band is attributed to the N%H stretching vibration. The C==N absorption in 4-MPipzcdtH capped Ag nanoparticles and complex [Ag(4-MPipzcdtH)](NO$_3$) has been observed at higher energies around 1467-1446 cm^{-1} in comparison to free ligand (1442 cm^{-1}). The rise in stretching frequency



(a) (b)

Figure 2 : SEM Micrographs of: (a) (Ag n4-MPipzcdtH) (1× 1) and (b) [Ag(4-MPipzcdtH)](NO3)



(a) (b)

Figure 3 : TEM Micrographs of capped silver nanoparticles (Ag n4-MPipzcdtH): (a) (0.5 × 1) and (b) (1.5×1)

has been attributed to a considerable double bond character of the bond in the complexes[11]. Observation of one band at 1018 cm^{-1} for ν_a(SCS) vibration and one band for ν_s(SCS) stretch at 670 cm^{-1} in the IR spectrum of capped silver nanoparticles suggests the symmetrical chelating bidentate mode of co-ordination to nanoparticles. Whereas observation of two bands in the region 969-1022 cm^{-1} (separated by more than 20 cm^{-1}) for ν_a(SCS) vibration and one band for ν_s(SCS) at 679 cm^{-1} in the IR spectrum of [Ag(4-MPipzcdtH)](NO$_3$) suggests the inequivalence of two sulphur atoms of >NCS$_2$ group for binding to silver (I). Observation of additional new bands in the region 388 – 354 cm^{-1} in 4-MPipzcdtH capped Ag nanoparticles and complex [Ag(4-MPipzcdtH)](NO$_3$) as compared to free ligand (4-MPipzcdtH) has been ascribed to Ag - S bonding. Whereas appearance of two bands at 840 cm^{-1} and 1379 cm^{-1} in the spectrum of [Ag(4-MPipzcdtH)](NO$_3$) shows the existence of ionic nitrate. Infrared spectra of 4-MPipzcdtH ligand and silver

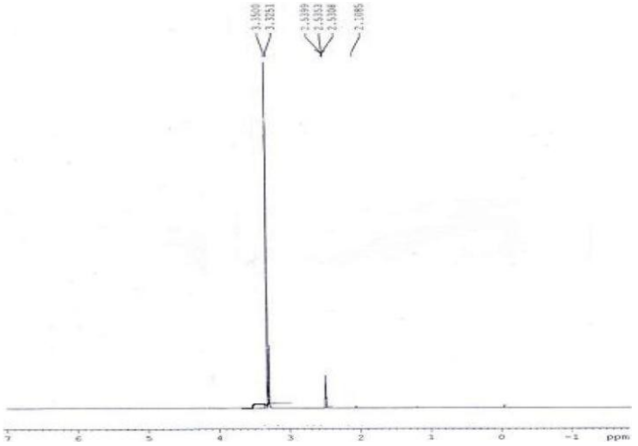


Figure 4 : 1H NMR Spectrum of (Ag n4- MPipzcdtH)

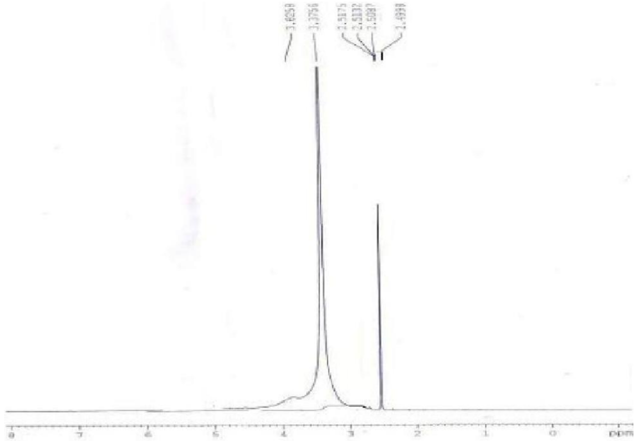


Figure 5 : 1H NMR Spectrum of [Ag(4-MPipzcdtH)](NO3)

TABLE 2 : ^{1}H NMR spectral data, δ (ppm) for 4-methylpiperazine-1-carbodithioic acid ligand, 4- MPipzcdtH capped silver nanoparticles (Ag n4-MPipzcdtH) and silver (I) complex ([Ag(4-MPipzcdtH)]NO3)

Sr. No.	Compound	NH	(2,6-)CH$_2$ (3,5-) CH$_2$	CH$_3$
1	4-MPipzcdtH	3.650 (s,1H)	3.740-3.787 (t, 8H: 2,3,5 and 6- CH$_2$)	2.960 (s, 3H)
2	Ag n4-MPipzcdtH (1.5×1)	3.600 (s, 1H)	3.251-3.350 (t, 4H) 2.531-2.540 (t, 4H)	2.109
3	[Ag (4-MPipzcdtH)]NO$_3$	3.826 (s,1H)	3.376 (t, 4H) 2.509-2.518 –(t, 4H)	2.500

nanoparticles capped with 4-MPipzcdtH, are similar in appearance except for difference in intensity of peaks of capped silver nanoparticles. This suggests that 4-MPipzcdtH remained adsorbed on silver nanoparticles surface. Similar behaviour has been observed for capped nanoaluminium[12] and capped nanosilver[13].

NMR studies

^{1}H NMR spectral study showed that particles are free from impurity. The proton NMR spectrum of free acid ligand, 4-MPipzcdtH shows the resonance signals: two overlapping triplets around δ 3.740-3.787 and a singlet at δ 2.960 ppm corresponding to four -CH$_2$- (2, 3, 5 and 6) and >N-CH$_3$ protons respectively[14]. Appearance of signal at δ 3.650 ppm has been attributed to proton resonance of N-H as a result of formation of a new N-H bond (structure A). The appearance of this downfield signal further suggests the presence of positive charge on nitrogen atom (deshielding the proton) as a result of proton binding with the nitrogen atom of CH$_3$-N< group yielding the zwitterionic form of the acid ligand. The overall downfield shift because of deshielding of protons of the methylene groups and a methyl group clearly revealed the presence of the +ve charge on the nitrogen atom at the 4th position of the 4-MPipzcdtH ligand. In the ^{1}H NMR spectra of 4-MPipzcdtH capped silver nanoparticles (Figure 4) and $(Ag(4\text{-}MPipzcdtH))_6(NO_3)_6$ complex (Figure 5), separate triplets due to 2,6 methylene (δ 3.73 - 4.00 ppm) and 3,5- methylene (δ 3.05-3.20 ppm) protons have been observed on the downfield and upfield side respectively in comparison to the free ligand. Johnson[15] has indicated that the double bond character of the C-N bond should result in hindered rotation of the S$_2$ group. Resolution of the two above said signals in the proton NMR spectra of the compounds under study in comparison to free acid may result because of the hindered rotation of the S$_2$ group of the 4-methylpiperazine-1-carbodithioate ligand. A signal at δ 3.600 – 3.826 ppm has been attributed to N – H bond, and a singlet at δ 2.109 – 2.500 ppm appears due to CH$_3$ protons of CH$_3$-N< group of 4-MPipzcdtH upon its co-ordination to the metal ion (TABLE 2).

XRD

Analysis of XRD pattern of 4-MPipzcdtH capped silver nanoparticles [(0.5×1), (1×1) and (1.5×1)] has revealed four distinct broad peaks appearing at 2 θ values as:

(1) (0.5×1) : 37.66°, 43.7°, 64.19° and 76.90°.

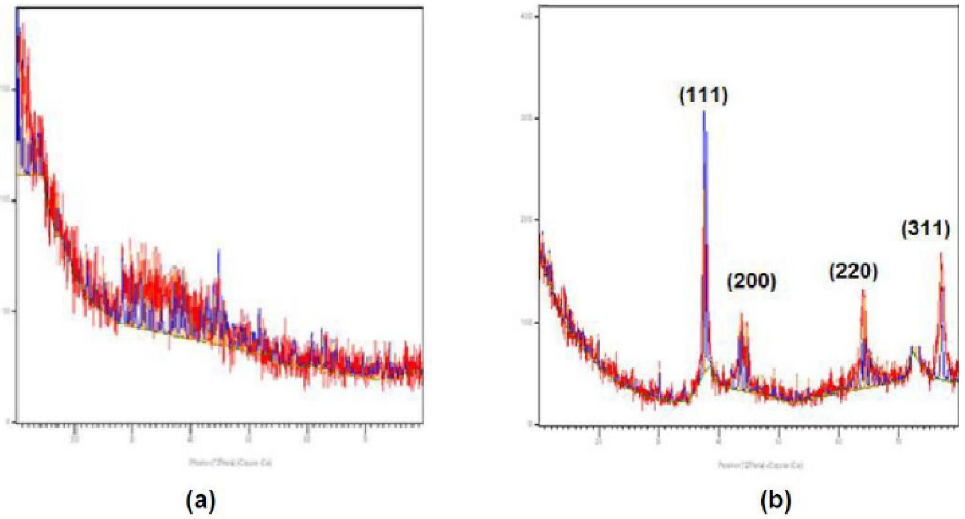


Figure 6 : XRD pattern of: (a) Ag(4-MPipzcdtH)](NO3) and (b) 4-MPipzcdtH capped silver nanoparticles (Ag n4- MPipzcdtH) (0.5×1)

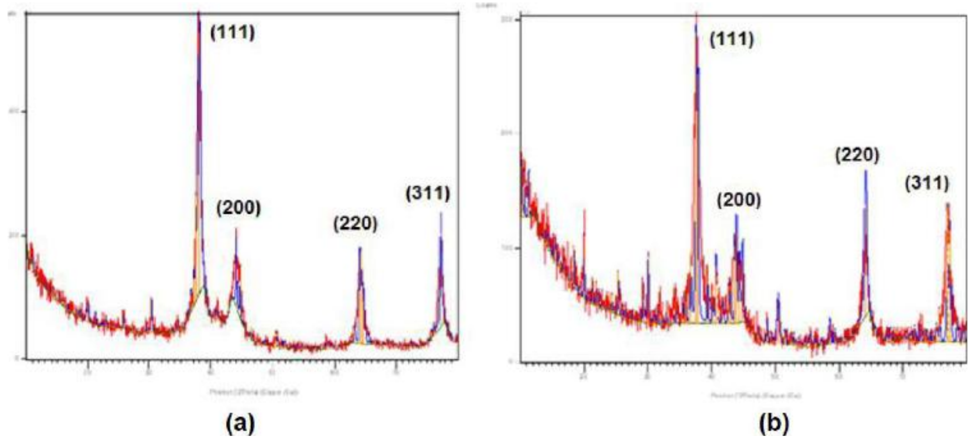


Figure 7 : XRD pattern of 4-MPipzcdtH capped silver nanoparticles (Ag n4-MPipzcdtH): (a) (1×1) and (b) (1.5×1)

(2) (1×1) : 37.65°, 44.04°, 64.31° and 77.18° and

(3) (1.5×1) : 37.56°, 43.86°, 64.08° and 77.06°. corresponding to crystalline planes which match with JCPDS card 4-0783[16] and hence have been indexed as (111), (200), (220) and (311) for respective 2 θ values (Figure 6,7). These correspond to face centered cubic structure (fcc) and hence 4-MPipzcdtH capped Ag nanoparticles consist of fcc structure.

From the XRD patterns, it is evident that reflection lines are quite broad for capped Ag nanoparticles. The broadening is caused by nanoparticle size. Hence, the average particles size was calculated using Debye Scherrer's equation[17] as:

$$Dp = \frac{k\lambda}{\beta_{1/2}\cos\theta}$$

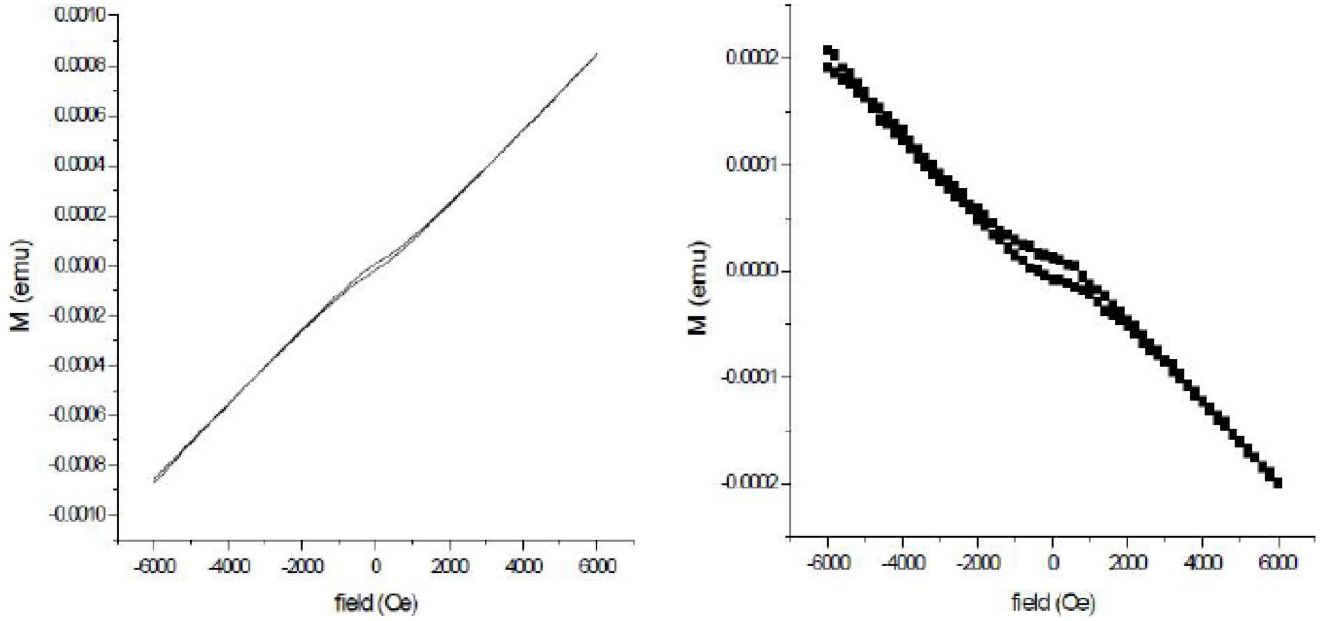
Where Dp (diffraction pattern) represents particle size in nm, k is the shape factor (usually taken as 0.94), λ is the X-ray wavelength (1.54 for Cu-K_α), θ is the Bragg2s angle in degrees and $\beta_{1/2}$ represents peak FWHM (full width at half maximum). The maximum intensity peak (111) was used to find the FWHM. The particle sizes calculated from Debye Scherrer's equation for (0.5×1), (1×1) and (1.5×1) ligand feed ratio are 9.89 nm, 6.37 nm and 5.95 nm respectively (TABLE 3). The particle size calculated from Debye Scherrer's equation is larger than those observed from TEM analysis (5 nm for (0.5×1) and 3 nm for (1.5×1) sample) (TABLE 4) which indicates that Scherrer's equation always tends to underestimate the real size of nanoparticles. This can be attributed to intrinsic stress developed in silver nanoparticles. The XRD pattern of [Ag(4-MPipzcdtH)](NO_3) complex does not show

TABLE 3 : XRD data of 4-MPipzcdtH capped silver nanoparticles and particles size obtained from TEM

Sr. No.	Compound (Ag n4-MPipzcdtH)	2 θ	Particle Size (Dp) nm (XRD)	Particle Size (nm) (TEM)
1	(.5×1)	37.66°	9.89	5
2	(1×1)	37.65°	6.37	-
3	(1.5×1)	37.56°	5.95	3

TABLE 4 : Effect of compound concerntration on lipase activity (μ mol/ml/min)

Compound Concentration mg (%)	Lipase Activity (μ mol/ml/min) of compounds				
	Control	Ag n 4-MipzcdtH (0.5×1)	(1×1)	(1.5×1)	[Ag (MPipzcdtH)](NO_3)
0 (0)	0.729	-	-	-	-
3 (.1)	-	1.032	1.097	1.050	1.116
6 (.2)	-	0.517	0.763	0.901	1.15
12 (.4)	-	0.299	0.305	0.318	0.374



(a) (b)

Figure 8 : Magnetic measurements of: (a) 4-MPipzcdtH capped silver nanoparticles (1×1) and (b) [Ag(4-MPipzcdtH)] NO3)

broad diffraction peaks (Figure 6a).

Magnetic susceptibility studies

Room temperature and magnetic field dependent susceptibility measurements of the 4-MPipzcdtH capped silver nanoparticles ((0.5×1), (1×1) and (1.5×1) sample) exhibit room temperature magnetic moment values in the range 1.71 - 1.73 BM. The μ_{eff} value reveals paramagnetic nature of the capped silver nanoparticles having silver in zero oxidation state ($d^{10}s^{1}$). The observed magnetic behavior of 4-MPipzcdtH capped silver nanoparticles resembles the magnetic behavior of thiol capped gold nanoparticles[18] and dithiol capped silver nanoparticles[19]. Hence, origin of the observed magnetism should be same as that observed in thiol capped gold nanoparticles. The complex [Ag(4-MPipzcdtH)](NO_3) exhibits room temperature magnetic moment value to be 0.02 BM corresponding to diamagnetic nature (d^{10}) (Figure 8).

Electronic spectral studies

Electronic/optical properties of silver reveal that it absorbs strongly in the visible region due to surface plasmon resonance[20] (SPR). Electronic absorption spectra of 4-MPipzcdtH capped silver nanoparticles

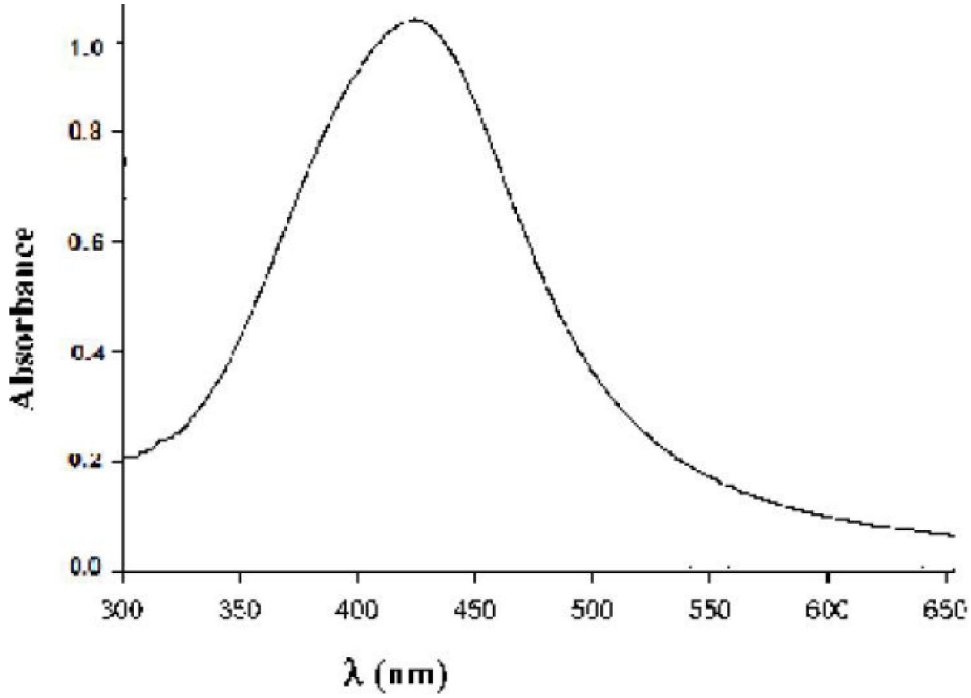


Figure 9 : Electronic absorption spectrum of 4-MPipzcdtH capped silver nanoparticles (Ag n4-MPipzcdtH) [(0.5×1)]

TABLE 5 : Effect of incubation time on lipase activity (µ mol/ml/min) in the presence of compounds

Time (minutes)	Lipase Activity (µ mol/ml/min) of compounds				
	Control	Ag n 4-MipzcdtH (0.5×1)	(1×1)	(1.5×1)	[Ag (MPipzcdtH)](NO$_3$)
5	0.714	1.69	1.73	1.83	1.89
10	0.729	0.299	0.305	0.318	0.374
20	0.750	1.22	1.26	1.28	1.32
30	0.838	1.30	1.48	0.979	0.985
40	0.899	1.45	1.65	0.773	1.14

[(0.5×1), (1×1) and (1.5×1)] revealed that for (0.5×1) sample (Figure 9) the surface plasmon resonance peak appeared at 430 nm, which is characteristic of silver nanoparticles[21]. Whereas for (1×1) and (1.5×1) samples, the absorption peak at 430 nm is weak. This can be attributed to the fact that with increase in initial ligand feed ratio the particle size decreases. Hence, SPR peak also diminishes.

Biological studies

4-MPipzcdtH capped silver nanoparticles ((0.5×1), (1×1) and (1.5×1) compound) and [Ag(4-MPipzcdtH)](NO3) complex exhibit inhibition in lipase activity to a large extent (0.299 – 0.374 µmol/ml/min) at a concentration 0.4% (12 mg). The nanoparticles with composition (0.5×1) show the maximum inhibition of lipase activity (0.299 µmol/ml/min) (TABLE 4). Effect of incubation time has also been studied for lipase assay in presence of above – said compounds at a concentration 0.4% (12 mg). TABLE 5 shows that maximum inhibition of lipase activity occurred at incubation time, 10 minutes.

So the optimum conditions for inhibition of lipase activity from 0.729 µmol/ml/min in control to 0.299 µmol/ml/min by 4-MPipzcdtH capped silver nanoparticles ((0.5×1), (1×1) and (1.5×1) compound) and [Ag(4-MPipzcdtH)](NO3) complex corresponds to a concentration of 0.4% (12 mg) at an incubation time of 10 minutes. It has been reported that heavy metal ions (Co^{2+}, Hg^{2+}, Ni^{2+}, Sn^{2+}, Ag^{+}[22]) drastically reduce/inhibit the lipase activity as compared to Zn^{2+} and Mg^{2+}.

CONCLUSIONS

In the present study stable silver nanoparticles have been prepared using 4-MPipzcdtH as capping agent. TEM studies revealed particle size of 3-5 nm which are well monodispersed. Magnetic studies showed that particles are paramagnetic in nature. XRD patterns indicated arrangement of silver nanoparticles with a face centered cubic (fcc) structure. Enzyme inhibition study of silver nanoparticles with different core diameters has exhibited reduction in lipase activity with decreasing ligand-metal feed ratio. Sample (0.5×1) showed maximum inhibition of lipase activity.

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