

Synthesis And Characterization of Nano-Sized Triphenylphosphine Capped Bis(4-Methylpiperazine-1-Carbodithioato)Zinc(II)

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ABSTRACT

Present study involves synthesis of and studies on a nanosized coordinate complex of 4-methylpiperazine-1-carbodithioate (4-MPipzcdt) with zinc(II), Zn(4-MPipzcdt)₂, using triphenylphosphine (PPh₃) as capping agent. EDAX spectrum of compound showed 40 wt% Zn; 6 wt% sulphur and 2 wt% phosphorus. SEM and TEM studies revealed needle shaped nanosized particles (8-12 nm). FT-IR spectrum showed bands at 1000 cm⁻¹ and 978 cm⁻¹ due to unsymmetrical binding of 4-MPipzcdt to Zn(II). Surface plasmon resonance of compound gave λ_{max} at 292 nm. XRD pattern showed sharp bands indicating crystalline nature of compound. Photocatalytic degradation of methyl orange was 60% with compound concentration of 1.5 mg/ml at pH 4. Increased inhibition in lipase activity (181.85 to 65.61 μmol/ml/min) in the concentration range of 100 -600 μg/ml has been observed.

Keywords: 4-MPipzcdt, PPh₃, Zn(II), TEM, nano.

1 INTRODUCTION

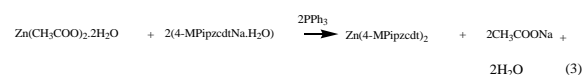
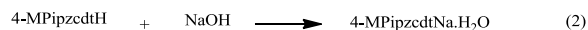
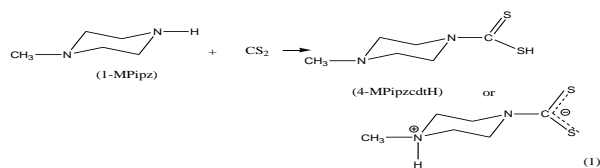
The synthesis of nanomaterials with varying size and shape and with different properties is a big challenge in front of scientists today. Zinc sulphide and zinc oxide nanoparticles with well-defined shapes (spherical, cuboidal) and dimensions (1-100 nm) have been prepared and reported to have optical, thermal and electrical properties. But as the nanoparticles have high surface to volume ratio they tend to agglomerate and form large clusters during synthesis. So it becomes important to control various particle-particle interactions during the course of reaction. To prevent the agglomeration of nanoparticles a number of long chain compounds have been used as chemical capping agents. Zinc sulphide (ZnS) and zinc oxide (ZnO) nanoparticles have been reported to be prepared using thioglycerol [1], thiourea[2,3], PVP[4-6],

trioctylphosphine oxide (TOPO) [7-9], tritonX-100 [10], allyl-phenyl dithiocarbamate[11], hexadecylamine (HDA) [12], CTAB [13] and glucose [14] as capping agents. ZnS nanoparticles have also been prepared by doping with manganese [15,16], using water oil emulsions [17] and NaCl flux [18]. ZnS nanoparticles coated on silica microspheres have also been reported [19]. Zinc based nano complex with tridentate donor schiff base has been recently reported [20].

2 RESULTS AND DISCUSSION

2.1 Synthesis and Characterization

The synthetic scheme for preparation of compound involves following steps (eqn 1,2 and 3).



Under present investigations synthesis of nanosized coordinate complex, bis(4-methylpiperazine-1-carbodithioato)zinc(II) using triphenylphosphine (PPh₃) as capping agent following bottom up approach has been undertaken. Use of PPh₃ has been made as it has wide range of chemistry acting as a good stabilizing agent. PPh₃ is unreactive towards organosulphur compounds such as thiols and thioethers. Metal dithiocarbamate complexes and their applications in biology, agriculture and industry are well documented. \

The interest in synthesis of nanosized metal complex has arisen with the hope to get improved results with respect to their applications in various fields.

SEM micrograph of compound revealed needle shape of particles (Figure 1).

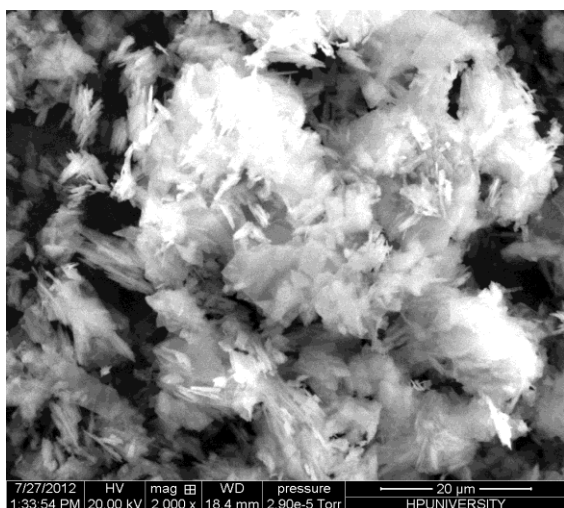


Figure 1. SEM micrograph of PPh₃ capped Zn(4-MPipzcdt)₂ nanoparticles.

EDAX spectrum (Figure 2) of complex inferred 40 wt% of Zn; 6 wt% of sulphur in addition to presence of phosphorus 2 wt%.

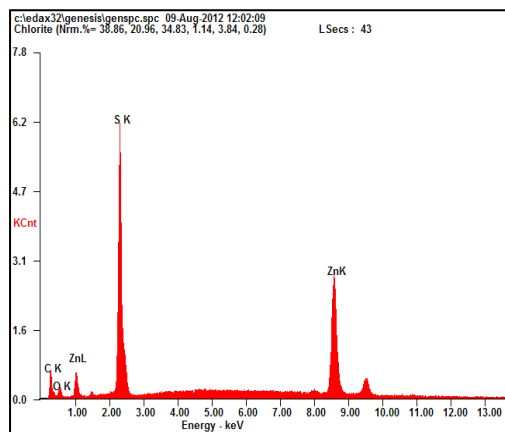


Figure 2. EDAX spectrum of PPh₃ capped Zn(4-MPipzcdt)₂ nanoparticles.

TEM study indicated nanosized particles with size range lying between 8-12 nm. (Figure 3).

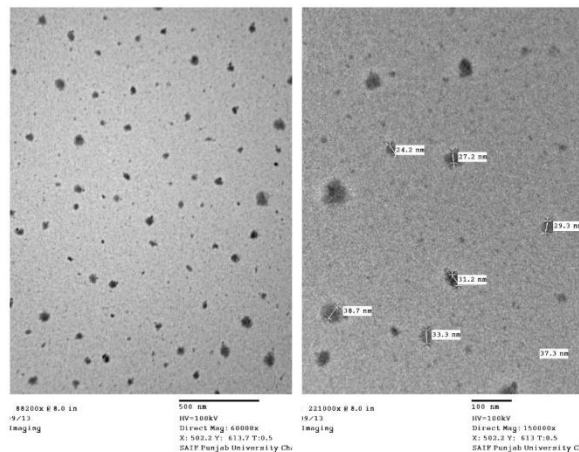


Figure 3. TEM image of PPh₃ capped Zn(4-MPipzcdt)₂ nanoparticles

In FT-IR spectrum of PPh₃ capped Zn(4-MPipzcdt)₂ compound two bands at 1000 cm⁻¹ and 978 cm⁻¹ have been observed for antisymmetric ν_a(SCS) vibration indicating unsymmetrical binding of 4-MPipzcdt ligand to Zn(II) ion. As expected the CS₂ symmetric stretch is not affected on complexation and is observed at 686 cm⁻¹. Additionally the compound showed absorptions at 1474, 1432, 1307, 1123 and 1023 cm⁻¹ which are ascribed to the ν(P-C) modes of vibrations of triphenylphosphine. These absorptions have been observed at about same stretching frequency as those for free PPh₃. Such an observation revealed the existence of PPh₃ as capping agent on Zn(4-MPipzcdt)₂.

XRD pattern of powder sample of PPh₃ capped Zn(4-MPipzcdt)₂ nanoparticles exhibited sharp peaks (Figure 4) at 2θ values of : 10.68° and 17.77°. Average particle size has also been calculated from XRD data using Debye Scherrer's equation (4).

$$D_p = \frac{k \lambda}{\beta_{1/2} \cos \theta} \quad (4)$$

where D_p (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 Bragg's angle in degrees and β_{1/2} represents peak FWHM (full width at half maximum).The particle size for the PPh₃ capped Zn(4-MPipzcdt)₂ complex has been calculated to be 12 nm.

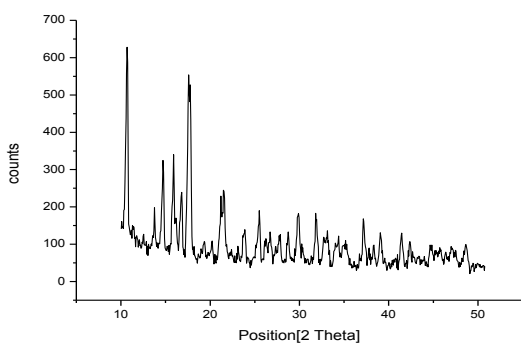


Figure 4. XRD spectrum of PPh₃ capped Zn(4-MPipzcdt)₂ nanoparticles.

PPh₃ capped Zn(4-MPipzcdt)₂ compound exhibited surface plasmon resonance peak at 292 nm (Figure 5).

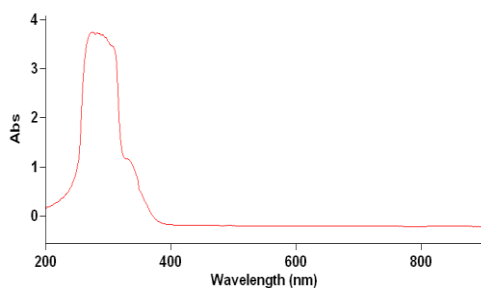


Figure 5. UV-visible spectrum of PPh₃ capped Zn(4-MPipzcdt)₂ nanoparticles.

Fluorescence spectrum of compound gave emission peaks at 454 nm and 647 nm when excited at 320 nm (Figure 6) This matches the data of emission spectrum of nitrogen and oxygen coordinating Schiff base complexes of Zn(II)[21].

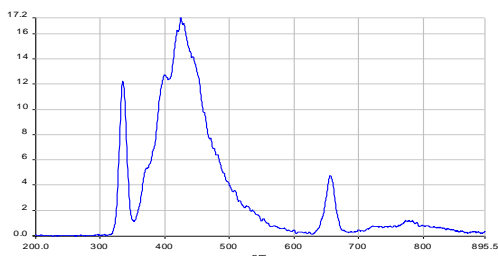


Figure 6. Emission spectrum of PPh₃ capped Zn(4-MPipzcdt)₂ nanoparticles.

2.2 Dye Degradation Study

Photocatalytic behavior of nanosized compound was analyzed by studying degradation of methyl orange in sunlight as well as dark. Degradation of dye was found to be 60%. Compound concentration used for this was

1.5mg/ml. In the experiment 75 mg of nano complex was added to 50 ml aqueous solution (10^{-5} M) of methyl orange dye. The mixture was kept at constant pH=4. The degradation behaviour was studied by varying compound concentration (Figure 7) as well as a function of time (Figure 8).

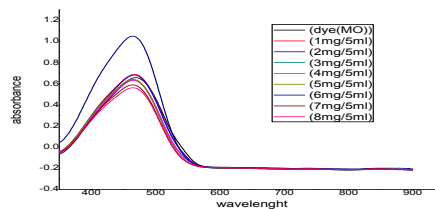


Figure 7. Photocatalytic degradation of methyl orange (1-8mg) by PPh₃ capped Zn(4-MPipzcdt)₂ nanoparticles.

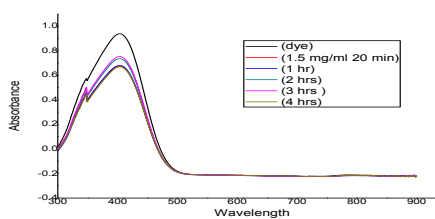


Figure 8. Photocatalytic degradation of methyl orange (1.5mg/ml, 20 min to 4 hrs) by PPh₃ capped Zn(4-MPipzcdt)₂ nanoparticles.

The absorbance of dye decreased from 0.964 to 0.421 with change of concentration between 1 to 8 mg/5ml and from 0.964 to 0.383 as a function of time (20 min to 3 hr). The experiment was performed in triplicate and average value has been given. It has been proposed that when aqueous solution of reaction mixture is irradiated to sunlight electron-hole pairs are generated which react with water to produce hydroxyl and superoxide radicals leading to disruption of conjugation in organic dye. The effect of transition metal ions on photocatalytic activity was the dynamics of electron-hole recombination and interfacial charge transfer.

2.3 Lipase Activity Assay

The PPh₃ capped Zn(4-MPipzcdt)₂ compound exhibited decreasing trend of inhibition of lipase (Steapsin) activity from 181.85 μ mol/ml/min to 65.61 μ mol/ml/min in the concentration range of 100 μ g/ml to 600 μ g/ml. The results have also been compared with normal compound Zn(4-MPipzcdt)₂ for which the activity decreases from 209.97 μ mol/ml/min to 157 μ mol/ml/min. Remarkable inhibition in lipase activity by both compounds in concentration range under study reveals that these compounds can act as good inhibitors

of lipase activity. Comparison of the data for lipase activity of the compounds indicates that nanosized compound exhibited larger decrease in activity as compared to normal compound.

2.4 *In Vitro* Antimicrobial Studies

Antimicrobial studies for the compounds 4-MPipzcdtNa.H₂O, Zn(4-MPipzcdt)₂ and nano coordination complex Zn(4-MPipzcdt)₂ have been screened against four bacterial strains, viz. *Escherichia coli*, *Pseudomonas pneumoneae*, *Staphylococcus aureus* and *Staphylococcus mutans*. Minimum inhibitory concentration (MIC) values lie in the range 250-500 µg/ml for 4-MPipzcdtNa.H₂O, 200 µg/ml for Zn(4-MPipzcdt)₂ and 50 µg/ml for PPh₃ capped Zn(4-MPipzcdt)₂. Comparison of MIC value of ligand and its metal compounds shows that the values decrease upon complex formation. PPh₃ capped Zn(4-MPipzcdt)₂

nanosized compound was more effective to inhibit the bacterial growth.

3 CONCLUSIONS

Preparation of nano coordination complex, i.e. PPh₃ capped Zn(4-MPipzcdt)₂ has been carried out using simple chemical method and particle size indicated by TEM studies is 8-12 nm. Compound has shown remarkably good antibacterial property against four bacterial stains viz. *Escherichia coli*, *Pseudomonas pneumoneae*, *Staphylococcus aureus* and *Staphylococcus mutans*. Compound has inhibited lipase activity to greater extent than normal complex. Degradation of dye methyl orange is also a promising application of the nano coordination complex.

REFERENCES

1. J. Nanda, S. Sapra and D. D. Sarma, Chem. Mater. 12, 1018-1024, 2000.
2. Z. Zhao, F. Geng, H. Cong, J. Bai and H.M. Cheng, Nanotechnology, 17, 4731-4735 2006.
3. M. Jayalakshmi and M. Mohan Rao, Journal of Power Resources, 157, 624-629, 2006.
4. Z. Deghani, S. Nazerdeylami, E. Saievar-Iranizad and M.H. Majles Ara, Journal of physics and Chemistry Solids, 72, 1008-1010, 2011.
5. L.Guo, S. Yang, C. Yang, P. Yu, J. Wang, W. Ge and G. K. L. Wong, Applied Physics Letters, 76, 2901, 2000.
6. C. Yang, P. Yu, J. Wang, W. Ge and G. K. L. Wong, Chem. Mater. 12, 2268-2274, 2000.
7. J. Joo, H. B. Na, T. Yu, J. H. Yu, Y. W. Kim, F. Wu, J. Z. Zhang and T. Hyeon, J. AM. CHEM. SOC. 125, 11100-11105, 2003.
8. Q. Zhao, L. Hou and R. Huang, Inorganic Chemistry Communications, 6, 971-973, 2003.
9. M. Dhanam, B. Kavitha, N. Jose and D. P. Devasia, Chalcogenide Letters, 6, 713 - 722, 2009.
10. D. C. Onwudiwe and P. A. Ajibade, Int. J. Mol. Sci, 12, 5538-5551, 2011.
11. B. Ludolph, M. A. Malik, P. O'Brien and N. Revaprasadu, Chem. Commun., 1849-1850, 1998.
12. P. A. Ajibade and J. Osuntokun, Hindawi Publishing Corporation Journal of Nanomaterials, 782526, 2014.
13. D. Mishra, P. Prabhakar, S. Lahiri, S.S. Amritphale and N.Chandra, Indian Journal of Chemistry, 52 A, 1591-1594, 2013.
14. U.S. Senapati, D.K. Jha and D. Sarkar, Research Journal of Physical Sciences, 7, 1-6, 2013.
15. B.S.R. Devi, R. Raveendran and A.V. vaidyan, Indian Academy of Sciences, 68, 679-687, 2007.
16. A. A. Khosravi, M. Kundu and B. A. Kuruvilla, Appl. Phys. Lett. 67, 17, 1995.
17. J. Xu and Y. Li, Journal of colloid and Interface Science, 259, 275-281, , 2003.
18. C. Lan, K. Hong, W. Wang and G. Wang, Solid State Communications, 125, 455-458, 2003.
19. N. A. Dhas, A. Zaban and A. Gedanken, Chem. Mater. 11, 806-813, 1999.
20. S.M.S.Haggag and I.A.M. Abdel-Hamid, J Therm Anal Calorim 119:737-746, 2015.
21. A.Guha, J. Adhikary, T.K. Mondal and D.Das, Indian Journal of Chemisrty, 50 A, 1463-1468, 2011.