P: ISSN No. 0976-8602 RNI No. UPENG/2012/42622 VOL.-10, ISSUE-2, April 2021
E: ISSN No. 2349-9443 Asian Resonance

Synthesis Characterization and Biological Studies of Some Mixed Ligand Complexes of Ti(IV) and Zr(IV) ion Complexes

Paper Submission: 05/04/2021, Date of Acceptance: 15/04/2021, Date of Publication: 26/04/2021

R. N. Sharma
Professor and Principal,
Dept. of Chemistry,
S.H.S. Govt. P.G. College,
Dhanapur, Chandauli, U.P., India

Yogesh Kumar Pandey
Ex Research Scholar,
Dept. of Chemistry,
K. N. Govt. P. G. College,
Gyanpur, Bhadohi, U.P., India

Rajnish Kumar Chauhan
Assistant. Professor,
Dept. of Chemistry,
P. G. College, Upardaha,
Baraut, Prayagraj, U.P., India

Soni Kumari
Assistant. Professor ,
Dept. of Botany,
P. P. K. College, Bundu,
Jharkhand, India

Abstract

Synthesis, spectral studies, characterization and biological activities of some mixed ligand complexes of Ti(IV) and Zr(IV) ions with 4-amino-5-mercapto-3-methyl-s-triazole(AMMSTH), pyridine and carbon disulphide are investigated. The complexes were characterized with the help of various physico-chemical studies such as micro analytical analysis, magnetic and conductometric measurement, infrared and electronic spectroscopic studies. All complexes were screened against *Aspergillus flavus*, a typical fungus. Octahedral configuration has been assigned for all complexes and also classified as mixed fungicides.

Keywords: Triazole, Complex , Fungicide, Physico-chemical, Ligand.

Introduction

The present studies deals the synthesis, characterization and biological studies of some mixed ligand Ti(IV) and Zr(IV) ions complex with 4-amino-5-mercapto-3-methyl- s-triazole (AMMSTH) as primary ligand. Pyridine and carbon sulphide are used as secondary ligand. Titanium and zirconium has shown versatile utility in chemistry[1-2] as well as industry. Triazole contains active NH, NH_2, C=S and H-N-C=S coordinating groups. The structures of all new chelates are elucidated on the basis of micro analytical analysis, magnetic and conductometric measurement, infrared and electronic spectroscopic studies. All complexes were screened against *Aspergillus flavus*, a typical fungus.

Review of the literature

Triazole derivatives have shown multidimensional coordinating abilities and biological activities[3-4]. A number of papers have been reported on metal triazole complexes[5-6]. Titanium has shown less bioactivity on comparison with Zirconium. Some times the biological activities increases on complexation with biological active ligand. Triazole derivatives are bulk reported bioactivities organic compound[7-8].

Objective of the study

Coordination complexes of transition metal have versatile application in various fields. Their uses towards industry as well as pharmaceutical applications are the main attraction for present studies. The study of shifting of vibrational band after complexation and their applications in elucidation of mode of bonding also attracts to work on characterization of complex. Entire world is facing a serious crisis as Covid-19 pandemic attack. It becomes more powerful with a black and white fungal attack. So, present studied on *Aspergillus flavus* may helpful to society.

Experimental

4-Amino-5-mercapto-3-methyl-s-triazole is prepared by some modified method reported in litrature[11]. The complexes are prepared by following methods. 1:2 molar 50 ml ethanolic solutions of metal salt and ligand were mixed slowly and then refluxed on hot plate magnetic stirrer at 80^0C up to 2 hours. The pH of solutions was adjusted at 6 using corresponding mineral acid and NaOH solution. It was evaporated up to 20 ml and then ice cooled. The complexes were separated out as a crystal. The all pyridyl and CS_2 containing complexes were prepared by filtrate of above solutions by adding one molar ratio in it. It was again refluxed at 80^0C up to one hour. The separated crystal were filtered, washed with ethanol and dried in air oven at 50^0C. All complexes were screened over

P: ISSN No. 0976-8602 RNI No. UPENG/2012/42622 VOL.-10, ISSUE-2, April 2021

E: ISSN No. 2349-9443 Asian Resonance

Aspergillus flavus, a typical fungus caused rot disease of pomegranates, dates, figs wilting of plant at 10, 100 and 1000 ppm concentration using cup plate method. The analytical and physical data of complexes has been shown in table-1. The spectral and biological data are shown in table-02.

Results and Discussion

The ligand (AMMSTH) form air stable solid complexes with Ti(IV) and Zr(IV) ion. It interacts with thione tautomeric form of ligand (fig 1) at pH ~6. All the complexes are soluble in DMF and DEMSO. The absorbed molar conductance values in DMF solutions lies in the range of 3.8- 6.19 ohm^{-1} cm^2 mol^{-1} indicating their non electrolytic nature[12].

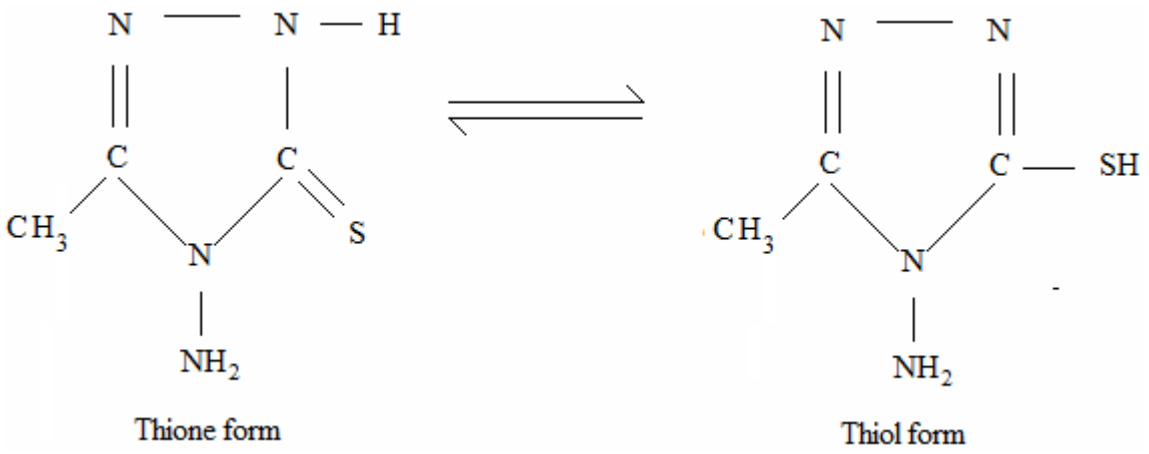

Fig.1. 4-Amino-5-Mercapto-3-Methyl-S-Triazole (AMMSTH)

The result of magnetic measurement showed the diamagnetic behavior as expected for d^0 complexes. The absorption due to $\pi \rightarrow \pi^*$ transition at 363.3 nm in electronic spectrum of ligand is blue shifted at 315-345 nm after complexation with Ti(IV) and Zr(IV) ions. However, no absorption absorbs at 400-800 nm. It shows that the metal ion has $(n-1)d^0ns^0$ electronic configuration as expected[13]. Important electronic bands are shown in Table-02.

Some IR spectral bands are shown in table-02. Ligand (AMMSTH) may form M-N and M-S bonding in complexes. So, it would be challenges to diagnose the bonding through N, S or both. vSH band at 2330 cm^{-1} of ligand is disappeared in all complexes indicates the involvement of sulphur atom in coordination[14]. AMMSTH showed vNH vibration[15-16] at 3940-3270 cm^{-1}. These bands are blue shifted after complexation suggests non involvement of imino nitrogen in metal bonding. It is also supported by shifting of thio amide bands (TAB) which plays characteristics diagnostic power in the region of 1580-910 cm^{-1}. Thio amide band I at 1580 cm^{-1}, II at 1315 cm^{-1}, III at 1030 cm^{-1} of ligand are blue shifted (~0-10 cm^{-1}) on coordination indicating the absence of bonding through imino nitrogen[17]. TAB IV plays diagnostics role to elucidate bonding through sulphur or nitrogen atom of this amide band. The red shifting of this band showed involvement of sulphur atom in bonding and blue shifting suggests the bonding through nitrogen atom. TAB IV are red shifted ~5 cm^{-1} in all Zr(IV) and 55-65 cm^{-1} for Ti(IV) complexes suggesting the metal ligand bonding through sulphur atom[18]. Non-ligand bond in all Ti(IV) and Zr(IV) complexes at 410 cm^{-1} are assigned as vTi-S and vZr-S. The bands at 405, 370 and 265 cm^{-1} are assigned as vTi-Cl and vZr-Cl mode of vibration[19]. Non ligand bands at 1605 and 635 are assigned as vPy in all pyridyl complexes[20] and at 1510 and 1150 cm^{-1} as vCS mode of vibrations in all CS_2 containing complexes. The non-ligand bands at 1130, 960, 490 cm^{-1} is assigned as mono dentate sulphato vibration in $[Zr(AMMSTH)_2(CS_2)(SO_4)_2]$ and $[Zr(AMMSTH)_2(Py)_2(SO_4)_2]$. Mono dentate vNO_3 bands[22] are assigned at 1510 and 1150 cm^{-1} in $[ZrO(AMMSTH)_2(CS_2)(NO_3)_2]$. All reported complexes were screened against for anti-fungal activities on *Aspergillus flavus* using cup plate methods by measuring the zone of inhabitation in nm after 76 hours of incubation at 42^0C and data were compared with carbendazim, a typical fungicide. $[ZrO(AMMSTH)_2(CS_2)(NO_3)_2]$ and $[Zr(AMMSTH)_2(Py)_2(SO_4)_2]$ showed 74.3% at 10 ppm and 72.5% at 1000 ppm respectively.

Conclusion

On the basis of normal coordinate analysis, all reported complexes of Ti(IV) and Zr(IV) ions have octahedral configuration. Since complexes contain more than one functional groups. So, all complexes may be classified as mixed fungicides[23]. $[ZrO(AMMSTH)_2(CS_2)(NO_3)_2]$ and $[Zr(AMMSTH)_2(CS_2)_2(SO_4)_2]$ may be reported as moderate fungicides.

P: ISSN No. 0976-8602 RNI No. UPENG/2012/42622 VOL.-10, ISSUE-2, April 2021
E: ISSN No. 2349-9443 Asian Resonance

Table-1: Analytical and physical data of complexes.

S. N.	Complexes/ (Colour)	Analytical data : Cal./(Found)				μ_{eff} (B.M.)	M.P. (in ^{0}C)	(ohm^{-1} cm^2 mol^{-1})
		M	C	H	N			
1.	$[Ti(AMMSTH)_2(Cl)_4]$ (White)	10.64 (9.85)	16.00 (15.31)	2.67 (1.91)	24.90 (23.97)	D.M.	172	4.16
2.	$[Ti(AMMSTH)(Py)(Cl)_4]$ (Brown)	12.03 (11.71)	24.13 (23.71)	2.76 (2.39)	17.59 (16.14)	D.M.	155	6.01
3.	$[Zr(AMMSTH)_2(Py)_2(SO_4)_2]$ (Broken white)	13.66 (13.51)	28.76 (28.39)	3.30 (3.21)	20.97 (20.23)	D.M.	241	6.19
4.	$[Zr(AMMSTH)_2(CS_2)_2(SO_4)_2]$ (Cream)	13.11 (12.19)	13.79 (13.61)	1.72 (1.63)	16.09 (15.27)	D.M.	206	7.19
5.	$[ZrO(AMMSTH)_2(CS_2)(NO_3)_2]$ (Yellowish white)	16.07 (15.23)	14.80 (13.96)	2.11 (2.01)	24.66 (24.31)	D.M.	216	3.87

Table-02: Spectral (nm and cm^{-1}) and biological data (ppm)

S.N.	Complexes	Electronic data (nm)	vCS/vPy	TAB IV	vNO_3/vSO_4	% Anti-fungal activities on *Aspergillus flavus* in ppm		
						10	100	1000
1.	AMMSTH	363.3	-	925 sb	-	—	—	—
2.	$[Ti(AMMSTH)_2(Cl)_4]$	342	-	860 m	-	22.3	26.10	29.10
3.	$[Ti(AMMSTH)(Py)(Cl)_4]$	345	1605 m 635 w	870 m	-	30.31	31.11	22.10
4.	$[Zr(AMMSTH)_2(Py)_2(SO_4)_2]$	315	1605 m 635 w	920 m	1130 m 960 w 490 w	36.10	70.10	72.50
5.	$[Zr(AMMSTH)_2(CS_2)_2(SO_4)_2]$	317	1510 m 1150 m	920 m	1130 m 960 w 490 w	25.10	43.70	67.20
6.	$[ZrO(AMMSTH)_2(CS_2)(NO_3)_2]$	321	1510 m 1150 m	920 m	1415 m 1305 m	74.30	65.20	60.70
7.	Carbendazim	-	-	-	-	84.8	88.7	98.6

References

1. *Praveen Kumar, Abhishek Agarwal, Anupam Kumar, Kavita and Alok Agarwal; Acta Ciencia indica, 25, 637 (2009).*
2. *N. Padmaja, M. Ravindar, M. Ramchary and S. Srihari; J. Indian Conc. Chem., 28, 8 (2011).*
3. *R. N. Pandey, Prashasti Pandey and R. N. Sharma; J. Ultra Sci., 20, 565 (2008)*
4. *Lina Mehta and Haula Parekh; J. Indian Chem. Soc., 63, 414 (1986).*
5. *N. Raman, S. J. Raja, J. Joseph and J. D. Raja; J. Chil. Chem. Soc., 52, 1138 (2007).*
6. *R. K. Dubey, U. K. Dubey and C. M. Mishra; Indian J. Chem., 47A, 1208 (2008).*
7. *R. Yadav and S. K. Srivastava; J. Indian Conc. Chem., 90, 28 (2011).*
8. *R. N. Sharma and Sanjay Singh; Asian Resonance, 4, 73 (2015).*
9. *S. Chandra and R. Kumar; Trant. Met. Chem., 29, 269 (2004)*
10. *A. P. Mishra and Anupoorna Tiwari; J. Indian Conc. Chem., 28, 01 (2011).*
11. *C. P. Joshsua and Annie Verghese; J. Indian Chem. Soc., 76, 759 (1990).*
12. *W. j. Greay; Coord. Chem. Rev., 7, 81 (1971).*
13. *R. N. Sharma; J. Chem. Tracks., 17, 134 (2015).*
14. *A. K. Sinha, P. D. Singh, B. N. Keshari and L. K. Mishra; J. Indian Chem. Soc., 65, 662 (1988).*
15. *Devendra Kumar, Anupama Bhaduria and R. C. Sharma; J. Indian Chem. Soc., 88, 472 (2011).*
16. *R. N. Sharma, Ashok Kumar Mishra, LaxmiKanth and SoniKumari; J. Ultra Chem., 16, 80 (2020)*
17. *Indrani Chakraborti; Asian J. Chem., 15, 1626 (2003).*
18. *B. Singh and H. N. Tiwari, H. H. Khan and R. N. Pandey; Indian J. Chem., 21A, 315 (1982).*

19. *R. J. Clark; "Halogen Chemistry", Academic press, London, 3 (1967).*
20. *R. N. Sharma; J. Chem. Tracks., 14, 220 (2012).*
21. *N. Tanaka, H. Sigi and J. Fujita; Bull Chem. Soc. Tap., 37, 640 (1964).*
22. *R. N. Sharma; J. Chem. Tracks., 16, 494 (2014).*
23. *R. N. Sharma, Rajnish Kumar Chauhan, Yogesh Kumar Pandey and alpana Kumari; J. Ultra Sci., 18, 383 (2006).*