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Vibrational and Antifungal Studies of Some Mixed Ligand Complexes of Ti(IV)ion



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Abstract

Some air stables non electrolytic complexes of Ti(IV)ion with substituted triazole have been prepared and characterized by various physico-chemical data based on micro analytical analysis, magnetic measurement, conductivity measurements, near and far infrared and electronic spectrophotometric studies. Various vibrational spectral bands (near & far) of ligand and complexes were studied and compared. All complexes were screened against *Aspergillus flavus* and classified as mixed fungicides. Tentative octahedral geometry has been assigned for all Ti(IV) complexes.

Keywords: Complexes, Ligand, Antifungal Activity, UV, IR Studies Vibrational Band.

Introduction

Complexes of certain metal specially transition metal complexes have powerful antimicrobial activities such as silver bandages for treatment of burns, zinc antiseptic creams, and metal clusters as anti-HIV drugs. Metal complexes are also used as antimicrobial and anti-fungal agent. Metal coordination complexes based on triazole continues to attract many researchers because of their wide pharmacological application like antifungal, antitumoral, antibacterial, antimicrobial etc¹⁻⁵. The present studies aim the synthesis, characterization and antifungal studies of titanium (IV) complexes with some mixed ligand 4-Amino-3-ethyl-S-triazole-5-thione (AEMTH) as primary ligand and pyridines as secondary ligand. Triazole has NH, NH₂, C=S and HNC=S donor groups. The stereo chemistry of all new complexes are tentatively assigned on the basis of micro analytical analysis, magnetic measurement, conductometric measurement, infrared, ultraviolet and visible spectrometric studies. All complexes were screened against a *flavus*, a typical fungus.

Review of Literature

Triazole derivatives have shown versatile coordinating abilities and bioactivities¹⁻². A number of papers have been reported on metal triazole complexes³⁻⁵. Titanium shows less bioactivity on comparison with other metals. But sometimes the bioactivity of some metals increases after complexation with bioactive ligand. Triazole derivatives are well studied multidimensional bioactive organic compound.

Objective of the Study

Coordination complexes of transition metal have versatile application in various fields. Their use towards pharmaceutical application are one of the important applications. So present studies are oriented towards the synthesis, structural characterization of Titanium complexes with some mixed ligands, interpretation of various near & far vibrational bands and their usefulness towards search of safe and effective fungicides.

Experimental

4-Amino-3-ethyl-S-triazole-5-thione has been prepared by some modified method reported in literature⁶. Ti(IV) complexes were prepared by following general method. [TiO(AEMTH)₃Br₂]H₂O, [TiO(AEMTH)₃]₂2H₂O and [TiO(AEMTH)₃ SO₄ H₂O] were prepared by refluxing 1:2 molar ethanol (50ml) solution titanium salts and AEMTH in hot plate magnetic stirrer for about 2 hours at 90° C. The pH of solution were adjusted near about 7 using corresponding mineral acids and concentrated sodium hydroxide solution. It was evaporated up to 10ml solutions and then ice cooled. The complexes were separated out as crystalline solids. It was filtered, washed and dried in air oven at 40°C. 10ml pyridine were added in above filtrate and again refluxed near about 1 hour and then evaporated up to dryness. It

was cooled and crystals were collected on whatman filter paper 41. It was also dried in air oven at 60°C. All air stable complexes were dried finally over anhydrous CaCl₂ in desiccator.

C, H and N were analyzed at CDRI Lucknow. Titanium was estimated gravimetrically. IR spectra of ligands and complexes were recorded with PerkinElmer model-577 spectrophotometer in the range of 4000-200 cm⁻¹. Samples were prepared as KBr pellets. Electronic absorption spectra of the complexes were recorded by Cary-17D automatic recording spectrophotometer. Molar conductance was measured using 10⁻³M solution in DMF on Wiss-Werkstätten Weiheim obb type LBR conductivity meter. The magnetic measurements were made on Gouy balance. All complexes were screened over *Aspergillus flavus*, a typical fungus causes rot disease of dates, figs wilting of plant (potato, pea, sun hemp, cotton etc) at 10, 100, 1000 ppm concentration using cup plate method. The analytical, physical, spectral and antifungal data are given in table-1.

Results and Discussion

The ligand (AEMTH) forms air stable solid complexes with Ti(IV) ions. It interacts with thion tautomeric form at pH 7. All complexes were soluble in DMF and found to be non-electrolytic in nature. All Ti(IV) complexes were diamagnetic as expected for d⁰ complexes⁷. The absorption at 255 nm in electronic spectrum of ligand (AEMTH) is assigned as π→π* mode of vibration. This band of ligand is blue shifted to (230-240) nm for all Ti(IV) complexes indicating the involvement of ligand in complexation. However no complexes absorption band between 400-800 nm showing (n-1)d⁰ns⁰ electronic configuration as expected for Ti(IV) ion⁷.

Important IR spectral bands and their assignments are presented in table-1 [TiO(AEMTH)₃Br₂]H₂O, [TiO(AEMTH)₃]2H₂O and [TiO(AEMTH)₃SO₄]H₂O showed strong broad band at 3430, 3460 and 3490 cm⁻¹ respectively are assigned as νH₂O mode of vibration⁸. Since a loss of weight appeared on heating up to 100°C indicating the presence of lattice layer water molecule at outside of coordination sphere in all these complexes⁹ except [TiO(AEMTH)₃SO₄]H₂O. So this [TiO(AEMTH)₃SO₄]H₂O complex has coordinated water.

Three bands at region of 3260-3110 cm⁻¹ in IR spectrum of ligand are assigned as νNH mode of vibrations¹⁰⁻¹¹. All these bands of ligand are either blue shifted or almost identical in all complexes indicating the non-involvement of νNH₂ group in complex formation. A sharp weak band appeared at 2450 cm⁻¹ in the spectrum of ligand is assigned as νSH mode of vibration¹². This ligand band is vanished in all complexes after complexation may be due to involvement of metal sulphur bonding in thione form of ligand. AEMTH contains thioamide group and it shows four characteristic thio amide bands¹⁴. This amide band I, II and III have dominating contribution of amino nitrogen atom appeared at 1570, 1410 and 900 cm⁻¹ in IR spectrum of AEMTH. This band is almost blue shifted 5 to 15 cm⁻¹ in all Ti(IV) complexes indicating the intactness of amino nitrogen in

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complexes¹⁴, but the thio amide band IV (755 cm⁻¹) of ligand has dominating contribution of thiol sulphur atom is red shifted (25 to 65 cm⁻¹) after complexation indicating the tautness of sulphur atom with Ti(IV) ion in bonding¹⁵ in all complexes.

The appearance of non-ligand bond in all pyridyl complexes at 1605 and 635 cm⁻¹ are assigned as νPy mode of vibrations and suggesting the presence of pyridine molecule as secondary ligand in all pyridyl complexes. The absorption at 1130, 960 and 490 cm⁻¹ are associated with [TiO(AEMTH)₄SO₄H₂O] and [TiO(AEMTH)₂(Py)₂SO₄] are assigned as unidentate νSO₄ vibrations¹⁶. The bands at 400 and 375 cm⁻¹ are assigned as νTiBr and νTiI mode of vibrations¹⁷ in [TiO(AEMTH)₃Br₂]H₂O & [TiO(AEMTH)₃]2H₂O respectively. Since only two vibrational bands appearance in far IR spectrum of above complexes suggesting the Trans occupation of halogens atom in complexation. The bands at 410 cm⁻¹ are assigned as νTi-S mode of vibrations¹⁸.

All Ti(IV) complexes were screened against antifungal activity on *Aspergillus flavus* using cup plate methods by measuring the zone of inhibition in nm and data were compared with carbendazin, a well-known commercial fungicide. [TiO(AEMTH)₂(Py)Br₂] showed 49.3% and [TiO(AEMTH)₃Br₂]H₂O 45% activities at 100 ppm respectively. It may be due to presence of Br and Py group.

Conclusion

On the basis of normal coordinate analysis, all Ti(IV) complexes have octahedral configuration. Since all complexes have more than one function groups in their structure, so all reported complexes are classified as mixed fungicides. [TiO(AEMTH)₂(Py)Br₂] and [TiO(AEMTH)₃Br₂]H₂O are found moderate fungicides.

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Table- 1
Physical Properties Analytical Major Spectral and Bioactivity Data of Complexes

S. No.	Complex, Colour, (M.P. °C)	% Analytical Data (Cal /Exp.)				% Zone of Inhabitation in ppm			uSH	Tab-IV	UV (nm)
		C	N	H	Ti	10	100	1000			
1	AEMTH	36.92	32.31	06.15	-				2450		255
2	[TiOBr ₂ (AEMTH) ₃] Thio Light Yellow (180°C)	23.50	20.56	04.24	07.32	25.3	45.0	43.1	_____	785	255
		22.61	20.12	4.03	6.93						
3	[TiOBr ₂ (AEMTH) ₂ (Py)] Brown (163°C)	27.71	17.41	03.73	08.51	20.3	42.3	49.3	_____	760	235
		26.24	17.21	3.49	07.64						
4	[TiOI ₂ (AEMTH) ₃] 2H ₂ O Yellow (193°C)	29.36	16.94	3.76	6.44	26.4	30.2	28.3	_____	720	230
		18.98	16.29	3.01	5.939						
5	[Ti I ₂ (AEMTH) ₂ (Py) ₂] Lemon Yellow (156°C)	30.00	15.56	03.61	06.65	28.4	21.5	35.1	_____	725	240
		29.81	15.23	03.41	06.26						
6	[Ti(O)(SO ₄)(AEMTH) ₃ H ₂ O] White (212°C)	27.51	24.07	04.87	06.75	21.9	38.4	36.1	_____	750	235
		27.01	22.85	04.31	06.44						
7	[Ti (O)(SO ₄)(AEMTH) ₂ (Py) ₂] Light Yellow (193°C)	37.51	19.45	04.52	08.32	26.3	26.1	31.3	_____	740	230
		37.11	19.24	04.32	08.01						
8	Carbendazine					93.1	94.1	97.8			