

Studies on Some Complexes of Zirconium (IV) with Substituted Triazoles having Thioamide Group

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Some air stable zirconium (IV) complexes with physiologically active substituted triazoles such as 3-(4-pyridyl)-4-phenyl-1,2,4-triazole-5-thione (PyPtTH), 4-amino-3-methyl-5-mercapto-*s*-triazole (AmMTH) and 1,2,4-triazole-3(5)-thiol (tTH) containing thioamide group have been prepared and characterised on the basis of various physico-chemical methods. All complexes have been isolated in ethanolic media and found to be diamagnetic in nature. In some cases the deprotonation of thiol tautomeric form of ligand occurs at pH = 8. The systematic shifts of all four thioamide bands are studied thoroughly and bonding through thione as well as thiol sulphur has been assigned. An octahedral structure for all complexes have been tentatively assigned.

INTRODUCTION

A large number of transition metal complexes of a variety of substituted triazoles have been synthesised¹⁻⁶. However, very little attempt has been made to isolate and characterise zirconium(IV) complexes with substituted triazoles having thioamide moiety⁷⁻⁹. In view of this, we undertook studies on synthesis and characterisation of Zr(IV) ion complexes of some physiologically active triazoles (Fig.1) such as 3-(4-pyridyl)-4-phenyl-1,2,4-triazole-5-thione (PyPtTH), 4-amino-3-methyl-5-mercapto-*s*-triazole (AmMTH) and 1,2,4-triazole-3(5)-thiol (tTH).

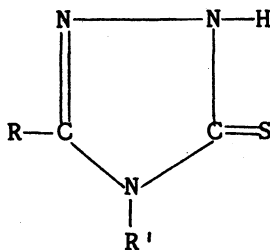


Fig. 1 (R = C₅H₅N, CH₃ or H and R' = C₆H₅, NH₂ or H)

EXPERIMENTAL

All chemicals used were of CP grade. The ligands were prepared by slightly modified methods reported in literature¹⁰⁻¹². The all Zr(IV) complexes were prepared in ethanolic media using a general method. Ethanolic metal salt (5 mmol) and ligand (15 mmol) solution were refluxed for about 2-3 hrs with few drops of corresponding mineral acids on a water-bath. The pH of the mixture was adjusted as desired using corresponding mineral acids and NaOH solution or pyridine. Then it was evaporated to 10 ml and cooled on ice-bath. The crystals separated were filtered, washed and dried over anhydrous CaCl₂ in vacuum desiccator. The magnetic measurements were made on Gouy balance at room temperature and calibration was done with mercury tetrathiocyanato cobaltate(II). IR spectra of the ligands and complexes were recorded in the range of 4000-200 cm⁻¹ on Perkin-Elmer-577 spectrophotometer using KBr pellets. The UV and visible spectra were recorded with the help of Beckmann DU-6 spectrophotometer in DMF.

RESULTS AND DISCUSSION

All the complexes were air stable and insoluble in common organic solvents such as MeOH, EtOH, CCl₄, C₆H₆ and petroleum ether but fairly soluble in DMF. The molar conductance measurement of complexes indicates the ionic nature of [ZrO(PyPtTH)₄Cl]Cl, [ZrO(AmMTH)₄Cl]Cl, [Zr(PyPtTH)₄(H₂O)₂](NO₃)₄ and [Zr(PyPtTH)₄(Py)₂](NO₃)₄. It was further supported by the qualitative analysis of sodium carbonate extract solution of complexes. The diamagnetic nature of all complexes suggests the d⁰ configuration as expected for Zr(IV) complexes. The analytical and physical data of the complexes have been shown in Table 1.

UV and visible spectra of complexes in DMF display very strong broad bands around 26,525, 30,525 and 30,303 cm⁻¹ for PyPtTH, AmMTH and tTH-complexes respectively which may be assigned to charge transfer bands¹³. However, no absorption was observed above 25,000 cm⁻¹ indicating d⁰-configuration of zirconium in all complexes⁷.

Major infrared spectral bands of interest have been given in Table-2.

The disappearance of νSH band at 2250, 2330 & 2340 cm⁻¹ in PyPtTH, AmMTH & tTH respectively after complexation indicate the absence of thiol tautomeric form of the ligand in the all complexes. The ligands AmMTH and tTH are deprotonated at pH ca 8 in [Zr(AmMTH)₂(AmMT)₄], [ZrO(AmMTH)₃(AmMT)₂] and Zr(tT)₄(Py)₂] which are supported by the reduction in splitting¹⁴ of νNH vibrations due to less availability of hydrogen atom for tautomerisation and considerable red shifting¹⁵ (ca. 100-120 cm⁻¹) of thioamide band IV. Moreover, the νNH bands were observed at 3260-3040, 3160 and

TABLE I
ANALYTICAL AND PHYSICAL DATA OF COMPLEXES

Complexes	Colour	pH of isolation	M.pt. (°C)	% Analysis-Found (Cal.)				Λ_m ($\text{Ohm}^{-1}\text{cm}^2\text{mole}^{-1}$)
				Zr	C	H	N	
$[\text{ZrO}(\text{PyPtTH})_4\text{Cl}]$	Light yellow	4	205	7.9 (7.6)	51.9 (52.3)	3.6 (3.2)	18.9 (18.8)	30.45
$[\text{Zr}(\text{PyPtTH})(\text{Py})\text{Cl}_4]3\text{H}_2\text{O}$	Golden yellow	6	220	14.7 (15.1)	34.9 (34.4)	3.2 (3.1)	11.3 (11.8)	1.69
$[\text{Zr}(\text{PyPtTH})_2\text{Cl}_4]$	Light yellow	7	250	12.8 (12.4)	42.0 (41.8)	2.8 (2.7)	15.0 (14.8)	3.40
$[\text{Zr}(\text{PyPtTH})_2\text{Cl}_4]2\text{H}_2\text{O}$	Lemon yellow	4	210	12.9 (12.3)	41.7 (42.1)	2.8 (2.7)	15.7 (15.1)	0.85
$[\text{ZrO}(\text{PyPtTH})(\text{H}_2\text{O})_2\text{Cl}_2]$	Pale Cream	7	250	20.1 (19.4)	33.8 (33.3)	2.8 (3.0)	11.2 (12.0)	0.92
$[\text{Zr}(\text{PyPtTH})_4(\text{Py})_2](\text{NO}_3)_4$	Golden Brown	7	250	6.7 (6.3)	51.5 (51.1)	3.1 (3.3)	18.4 (18.3)	104.51
$[\text{Zr}(\text{PyPtTH})_4(\text{H}_2\text{O})_2](\text{NO}_3)_4$	Brownish yellow	5	210	6.5 (6.8)	46.9 (46.7)	3.5 (3.3)	16.9 (16.8)	105.20
$[\text{Zr}(\text{PyPtTH})_2(\text{Py})_2(\text{H}_2\text{O})_2](\text{NO}_3)_4$	Lemon yellow	2	140	9.3 (8.8)	42.1 (41.5)	2.9 (3.1)	18.4 (18.6)	107.50
$[\text{Zr}(\text{AmMTH})(\text{H}_2\text{O})_3(\text{SO}_4)_2]$	White	7	192	20.1 (19.5)	8.2 (7.7)	2.5 (2.6)	11.6 (12.0)	5.05

Complexes	Colour	pH of isolation	M.pt. (°C)	% Analysis-Found (Cal.)				Λ_m ($\text{Ohm}^{-1}\text{cm}^2\text{mole}^{-1}$)
				Zr	C	H	N	
$[\text{Zr}(\text{AmMTH})_2(\text{AmMT})_4]$	Yellowish White	8	205	11.1 (10.5)	25.9 (26.6)	1.6 (1.4)	38.7 (39.7)	2.75
$[\text{ZrO}(\text{AmMTH})_3(\text{AmMT})_2]$	Yellowish White	8	210	12.8 (12.2)	22.6 (22.2)	2.2 (2.4)	38.4 (37.6)	6.70
$[\text{ZrO}(\text{AmMTH})_4\text{Cl}]\text{Cl}$	White	4	200	13.8 (13.3)	20.9 (20.6)	3.2 (3.4)	32.9 (32.1)	27.40
$[\text{Zr}(\text{tT})_4(\text{Py})_2]$	White	8	205	14.8 (14.2)	33.2 (33.7)	1.4 (1.3)	30.5 (30.6)	3.24
$[\text{Zr}(\text{tTH})_2(\text{H}_2\text{O})_2(\text{SO}_4)_2]$	Light yellow	4	250	17.7 (17.5)	8.9 (9.2)	1.8 (1.9)	16.4 (16.2)	15.60

TABLE 2
KEY IR BANDS (cm^{-1}) OF ZIRCONIUM (IV) COMPLEXES

Complexes	$\nu_{\text{H}_2\text{O/Py}}$	ν_{NH}	ν_{SH}	Thioamide Bands				$\nu_{\text{Zr}=\text{O}}$
				I	II	III	IV	
PyPtTH	—	3060 mb	2250 wb	1480 s	1290 s 1240 m	1090 m	785 m	—
$[\text{ZrO}(\text{PyPtTH})_4\text{Cl}]\text{Cl}$	—	3080 ms	—	1485 s	1290 m 1270 s	1080 m	770 s	1015 m 640 m
$[\text{ZrO}(\text{PyPtTH})(\text{H}_2\text{O})_2\text{Cl}_2]$	3500–3400 mb	3130 wb	—	1490 ms	1235 m	1080 ws	765 s	1015 s
$[\text{Zr}(\text{PyPtTH})_4(\text{H}_2\text{O})_2](\text{NO}_3)_4$	3500–3420 sb	3110 mb	—	1510 m	1290 m 1280 s 1230 ms	1070 ws 1065 m	765 m	645 m
$[\text{Zr}(\text{PyPtTH})_4(\text{Py})_2](\text{NO}_3)_4$	3500 ws	3360 mb	—	1485 s	1270 s	1080 w	765 m	—
$[\text{Zr}(\text{PyPtTH})_2\text{Cl}_4] \cdot 2\text{H}_2\text{O}$	3470 mb	3080 m	—	1495 s	1275 s 1220 s	1075 m	765 m	—
$[\text{Zr}(\text{PyPtTH})_2\text{Cl}_4]$	—	3080 m	—	1482 s	1275 s 1270 s	1080 ms	770 s	—
$[\text{Zr}(\text{PyPtTH})(\text{Py})\text{Cl}_4] \cdot 3\text{H}_2\text{O}$	3500–3200 sb	3160 mb	—	1498 m	1230 s	1065 ws	765 m	—
$[\text{Zr}(\text{PyPtTH})_2(\text{Py})_2(\text{H}_2\text{O})_2](\text{NO}_3)_4$	3500–3400 mb	3070 m	—	1480 s	1220 sb 1275 m 1270 m	1070 m	765 m	—
AmMTH	—	3260 s 3180 m 3110 s 3040 mb	2330 wb	1500 s	1240 w 1355 s 1265 m	1050 s 990 s	925 sb	—

Complexes	$\nu_{\text{H}_2\text{O/Py}}$	ν_{NH}	ν_{SH}	Thioamide Bands				$\nu_{\text{Zr}=\text{O}}$
				I	II	III	IV	
$[\text{Zr}(\text{AmMTH})_2(\text{AmMT})_4]$	—	3280 s 3180 s 3115 vs	—	1515 ms	1320 vs 1295 ws 1270 ws	1040 m 985 ms	825 m	—
$[\text{ZrO}(\text{AmMT})_2(\text{AmMTH})_3]$	—	3285 s 3190 w 3120 vs	—	1505 ms	1320 vs 1295 ws 1270 w	1040 ms 985 ms	815 m	1020 m 640 ms
$[\text{ZrO}(\text{AmMTH})_4\text{Cl}]\text{Cl}$	—	3280 s 3190 w 3120 vs 3060 w	—	1525 ms	1320 m 1295 ws 1270 w	1040 ms 985 ms	920 m	1020 w 645 w
$[\text{Zr}(\text{AmMTH})(\text{H}_2\text{O})_3(\text{SO}_4)_2]$	3500–3420 mb	3285 s 3195 w 3120 vs 3060 w	—	1525 m	1320 vs 1295 vs 1270 w	1040 m 985 ms	910 m	—
tTH	—	3160 m	2340 s	1485 s	1295 m 1250 s	1055 s	840 s	—
$[\text{Zr}(\text{TH})_2(\text{H}_2\text{O})_2(\text{SO}_4)_2]$	3600–3440 mb	3200– 3060 mb	—	1500 ms	1285 m 1250 ms	1030 m	830 w	—
$[\text{Zr}(\text{TT})_4(\text{Py})_2]$	3320 mb	3190 ws 3120 s 3070 m	—	1510 s	1275 m 1240 m	1040 s	710 vw	—

3060 cm^{-1} in AmMTH, tTH and PyPtTH respectively were blue shifted in almost all complexes indicating the absence of bonding through amino nitrogen. The systematic shifts in four thioamide bands^{16,17} indicate the coordination of the ligand through sulphur. The thioamide band I has been observed about 1480–1500 cm^{-1} in the ligands having mixed contribution from δCH , δNH and $\nu\text{C}=\text{N}$ are blue shifted (ca. 5–10 cm^{-1}). However, other three thioamide bands of ligands have been observed at (1355, 1292 \pm 3, 1245 \pm 5), (1090, 1052 \pm 3) and (925, 840 and 785) cm^{-1} are identical or red shifted (ca. 5–20 cm^{-1}) with reduced intensity in all complexes indicating the increase of CN bond order and decrease in CS bond order on coordination¹⁸. But 100–120 cm^{-1} red shifting of thioamide band IV of $[\text{Zr}(\text{AmMTH})_2(\text{AmMT})_4]$, $[\text{ZrO}(\text{AmMTH})_3(\text{AmMT})_2]$ and $[\text{Zr}(\text{Py})_2(\text{tT})_4]$ suggests the bonding through deprotonated thiol sulphur¹⁹.

The presence of ionic nitrate is indicated by the appearance of very strong band at 1350 \pm 5 cm^{-1} and a medium band at 830 cm^{-1} in all nitrate complexes²⁰. The fundamental sulphato mode of vibrations ν_1 , ν_2 , ν_3 and ν_4 are observed at (972 \pm 5, 1002), 940 \pm 5, 940 \pm 5, 1118 and 604 \pm 5 cm^{-1} respectively indicating the presence of monodentate sulphato group²¹ $\nu(\text{Zr}=\text{O})$ mode of vibration are observed at 1020 \pm 5 and 640 \pm 10 cm^{-1} .

Some new bands are observed in far IR spectra of complexes. The new bands observed at (545 \pm 5, 300), (470 \pm 5) and (405, 370, 325) cm^{-1} are assigned as νZrO , νZrPy and νZrCl respectively. Moreover, the *cis* and *trans*²² octahedral structure of light yellow (pH = 7) and lemon yellow (pH = 4) isomeric complexes having formula $[\text{Zr}(\text{PyPtTH})_2\text{Cl}_4]_n\text{H}_2\text{O}$ has been assigned on the basis of far IR spectra. Thus, on the basis of above studies an octahedral structure can be tentatively be assigned to these complexes.

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