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Studies on Some Complexes of Pd(0), Pt(0), Rh(I) and Zr(IV) with Physiologically Active 4-Amino-5-Mercapto-3-Methyl-s-Triazole

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Some new complexes of Pd(0), Pt(0), Rh(I) and Zr(IV) ions with 4-amino-5-mercapto-3-methyl-s-triazole (AmMTH) have been prepared and investigated using various physico-chemical methods. Pd(0) and Pt(0) complexes have been prepared from Malatesta compounds $Pt(P\emptyset_3)_4$ and $Pd(P\emptyset_3)_4$ and Rh(I)-complexes are prepared starting from Wilkinson's catalyst $(P\emptyset_3)_3RhCl$ in benzene medium. However, Zr(IV) complexes have been isolated in ethanolic medium. Tetrahedral structure of Pd(0), Pt(0), square- planar for Rh(I) and distorted octahedral structure for Zr(IV) complexes have been assigned reasonably using various physico-chemical data.

INTRODUCTION

Coordination complexes of substituted triazoles with a number of metal ions have been studied by several workers [1-3]. However, comparatively less work has been done on Pd(0), Pt(0), Rh(I) and Zr(IV) ions with substituted triazoles having thioamide groups. In continuation of our earlier work, the present paper deals with the preparation and characterisation of the complexes of Pd(0), Pt(0), Rh(I) and Zr(IV) ions with physiologically active 4-amino-5-mercapto-3-methyl-s-triazole (AmMTH) (Fig. 1) on the bais of magnetic, conductometric, microanalytical, IR, UV and visible spectral studies.

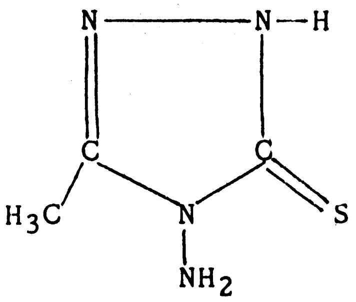

Fig.1. 4-Amino-5-mercapto-3-methyl-s-triazole (AmMTH)

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EXPERIMENTAL

All chemicals used were of CP grade. The ligand was prepared by slightly modified method reported in literature[4]. The Zr(IV) complexes were prepared in ethanolic media using a general method. Ethanolic metal salts (5 mmole) and ethanolic ligand (15 mmole) solution (1 : 1) were refluxed for about 2–3 h with few drops of corresponding mineral acids on a water-bath. But Pd(0), Pt(0) and Rh(I) complexes were prepared from $[Pd(PØ_3)_4]$, $[Pt(PØ_3)_4]$[5] and $[Rh(PØ_3)_3Cl]$[6] respectively. About 1 : 1 benzene solution mixture of ligand and above complexes was refluxed for about 2 h. 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 out were filtered, washed and dried over anhydrous $CaCl_2$ in vacuum desiccator. The magnetic measurements were made by means of Gouy balance at room temperature and calibration was done with mercury tetrathiocyanato cobaltate(II). IR spectra of the ligand 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-5 Spectrophotometer in DMF.

RESULTS AND DISCUSSION

All complexes were air stable and insoluble in common organic solvents such as benzene, acetone, chloroform, methanol, ethanol and petroleum ether but fairly soluble in DMF. The molar conductance measurement of complexes indicates the ionic nature of $[Zr(Py)_2(AmMTH)_4](NO_3)_4$ and $[Zr(AmMTH)_3](NO_3)$. It was further supported by the qualitative analysis of sodium carbonate extract solution of complexes. The diamagnetic nature of all Pd(0), Pt(0), Rh(I) and Zr(IV) complexes suggests the d^{10}, d^{10}, d^8 and d^0 configuration as expected respectively. The oxidation state of Pd(0), Pt(0) and Rh(I) complexes was confirmed by iodiometric titration. The complexes, their analytical and physical data have been shown in Table-1.

Electronic spectra of all Pd(0), Pt(0), Rh(I) and Zr(IV) complexes showed absorption maxima in the range of 28900–30525 cm^{-1}. The strong absorption is expected to be ligand-metal charge transfer bond[7, 8]. However, no absorption has been observed above 25000 cm^{-1} in Zr(IV) complexes indicating d°-configuration[9].

The presence of νNH and νNH_2 mode of vibrations[10] at 3270(m), 3180(s), 3110(s) and 3040(mb) cm^{-1} and νSH vibrations[11] at 2340(w) cm^{-1} in the IR spectrum of ligand indicate the existence of thione as well as thiol form of the ligand. The νNH and νNH_2 vibrations are blue shifted (*ca.* 5–10 cm^{-1}) in all Pd(0), Pt(0), Rh(I) and Zr(IV) complexes except $[Zr(AmMT)_3]NO_3$ indicating the absence of bonding through imino nitrogen. However, these bands are red shifted towards higher to lower wave number (*ca.* 10–20 cm^{-1}) with reduced splitting suggesting the bonding through amino nitrogen and deprotonation[12] of ligand in $[Zr(AmMT)_3]NO_3$ which may be due to less availability of H atom. These results are further supported by the systematic shifting of ligand bonds at 1610(ms) (δNH), 1250 m (ρ_wNH) and 733 s (τNH) cm^{-1}. The disappearance of νSH band after complexation indicates the bonding through thione tautomeric form of sulphur. The thioamide bands-I as observed at 1580 cm^{-1} in 4-amino-5-mercapto-3-methyl-s-triazole having mixed contribution from δCH, δNH and νCN are blue shifted and other three thioamide bands at 1315, 1050 and 825 cm^{-1} respectively are red shifted (*ca.* 10–20 cm^{-1}) in all complexes indicating the increase of CN bond order and decrease in CS bond order on coordination[13-15]. But thioamide band-I is red shifted towards lower frequencies (10 cm^{-1}) in [Zr(AmMT)$_3$]NO$_3$ and thioamide band-IV is almost identical with reduced intensity which may be due to equal interaction of CS and CN bond order suggesting the bonding through nitrogen as well as sulphur atom of thioamide group[16].

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF COMPLEXES

Compound (Colour)	m.p. (°C)	pH of isolation	% Analysis : Found (Calcd) M	C	H	N
[Pd(PØ$_3$)$_2$(AmMTH)$_2$] (Golden yellow)	200	7	12.22 (11.98)	56.93 (56.61)	4.59 (4.67)	12.41 (12.56)
[Pt(PØ$_3$)$_2$(AmMTH)$_2$] (Brownish yellow)	215	7	19.51 (19.99)	51.11 (51.51)	4.62 (4.31)	11.64 (11.39)
[Rh(PØ$_3$)(AmMTH)$_2$Cl] (Light yellow)	210	7	16.24 (16.48)	46.21 (46.08)	4.29 (4.32)	18.05 (17.92)
[Zr(AmMTH)$_4$(Py)$_2$](NO$_3$)$_4$ (Yellowish white)	240	7	19.40 (19.02)	29.82 (30.04)	3.10 (3.29)	30.34 (30.22)
[ZrO(AmMTH)$_2$(Py)(NO$_3$)$_2$] (Yellowish white)	220	7	16.15 (16.06)	23.51 (23.21)	3.21 (3.09)	26.75 (27.07)
[ZnO(AmMTH)$_3$(NO$_3$)$_2$] (White)	190	6	14.61 (14.72)	17.82 (17.41)	2.70 (2.92)	31.71 (31.68)
[Zr(AmMTH)$_2$(NO$_3$)$_4$] (White)	205	6	15.10 (15.23)	12.21 (12.00)	2.36 (2.03)	28.07 (28.14)
[Zr(AmMT)$_3$](NO$_3$) (White)	200	8	17.12 (16.98)	20.11 (20.06)	3.13 (2.86)	33.92 (33.76)
[Zr(AmMTH)$_4$(SO$_4$)$_2$] (Light yellow)	205	7	12.93 (12.88)	19.91 (20.23)	3.61 (3.42)	31.72 (31.56)

The bands observed at 1620, 1598, 1435 and 540 cm^{-1} are assigned due to triphenyl phosphine (PØ$_3$) mode of vibrations and suggesting the tactness of PØ$_3$ in Pd(0), Pt(0) and Rh(I) complexes. The ν(Zr=O)[17] is observed at 1020, 505 ± 5 and 475 cm^{-1} in all oxozirconium complexes and ν(Zr–Py)[18] mode of vibrations are assigned at 3460, 3420, 670, 475 and 252 cm^{-1} in all pyridyl complexes. The fundamental sulphato mode of vibrations such as ν_1, ν_2, ν_3 and ν_4 is observed at 975, 490, 1118 and 610 cm^{-1} respectively in [Zr(AmMTH)$_4$(SO$_4$)$_2$] suggesting the presence of monodentate sulphato group[19]. The nitrato mode of vibrations had been assigned at 1350 ± 5 and 850 cm^{-1} in the spectra of [Zr(AmMTH)$_4$(Py)$_2$](NO$_3$)$_4$ and [Zn(AmMT)$_3$]NO$_3$

and 1115 ± 5, 995 and 613 cm^{-1} in all other nitrato complexes. The separation of two higher bands at about 500 and 120 cm^{-1} in these two types of nitrato complexes, suggesting the ionic nitrate in $[Zn(AmMTH)_4(Py)_2](NO_3)_4$ and $[Zn(AmMT)_3]NO_3$ and unidentate in all other nitrato complexes[20].

The far infrared spectra of the complexes reveal some new bands at 415 ± 5 and 357 cm^{-1} ν(Zr–S) and 420 cm^{-1} ν(Zr–N). The ν(Rh–P), ν(Rh–S) and ν(Rh–Cl) are assigned at 380, 355 and 290 cm^{-1} and ν(Pt–P) and ν(Pt–S) are at 428 and 328 cm^{-1} respectively.

Thus, on the basis of above studies, the distorted octahedral structure for Zr(IV), square-planar for Rh(I) and tetrahedral for Pd(0) and Pt(0) complexes have been tentatively assigned.

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