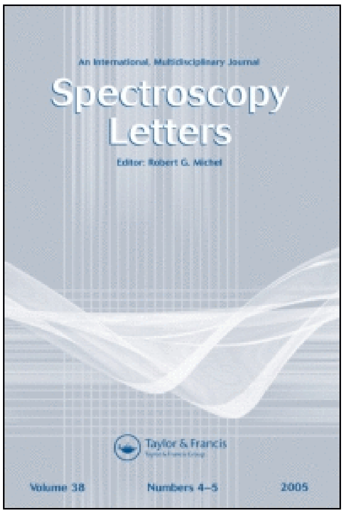

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COMPLEXATION REACTIONS OF Rh^{III}, Ru^{III}, Pd^{II}, AND Pt^{II} WITH 1H-1,2,4-TRIAZOLE-3-THIOL

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COMPLEXATION REACTIONS OF Rh^{III}, Ru^{III}, Pd^{II}, AND Pt^{II} WITH 1H-1,2,4-TRIAZOLE-3-THIOL

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ABSTRACT

New complexes of Rh^{III}, Ru^{III}, Pd^{II} and Pt^{II} with 1H-1,2,4-triazole-3-thiol have been prepared and characterized by spectroscopy [IR, UV-Vis, ^{1}H NMR and ^{13}C NMR] and microanalysis. The results are consistent with the general formula $M(HTAZ)_2Cl\cdot(H_2O)$, [$M = Rh^{III}$ and Ru^{III}], $M(HTAZ)_2(H_2O)_2$ and [$M = Pd^{II}$ and Pt^{II}].

Key Words: Complexes of Rh^{III}, Ru^{III}, Pd^{II}, and Pt^{II}; Spectroscopy [IR, UV-Vis, ^{1}H NMR and ^{13}C NMR]; Microanalysis

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INTRODUCTION

Recently, there has been considerable interest in chemistry of the metal complexes of triazole compounds because of its biological application such as antifungal, antibacterial,[1,2] antitumor,[3] anti-inflammatory, antimycobacterials[4] and anticonvulsant.[5] Therefore understanding the interaction of the triazole ligands with metal ion commonly present in living systems yield important information for understanding their biological activity.

In the present work we have synthesized new complexes of Rh^{III}, Ru^{III}, Pd^{II} and Pt^{II} with 1H-1,2,4-triazole-3-thiol as ligand. The prepared complexes were characterized using a combination of various physicochemical techniques.

EXPERIMENTAL

All chemicals used in the present investigation are of analytical grade and were used without further purification. Elemental analysis was performed by the Micro-analytical Unit at King Abdul-Aziz City for Science and Technology, Riyadh, Saudi Arabia. UV-Vis spectra were recorded on a Shimadzu UV-1650 PC spectrophotometer. Infrared spectra were measured as KBr pellets on a Perkin-Elmer 883 spectrophotometer. NMR spectra were determined on a Joel-400 spectrometer in DMSO-d_6 as solvent. The complexes are insoluble in most of the known solvent; they are soluble in DMF and DMSO only and for this reason the approximate method has been used to determine the molecular weight to the complexes that is Rast's method using camphor as solvent.[6]

General Method for Preparation of the Complexes

A quantity of 2.5 mmol of the corresponding MCl_3 ($M = Rh^{III}$, and Ru^{III}) was dissolved in 30 mL ethanol and added dropwise to 10 mL of an ethanolic solution of the ligand (7.5 mmol). The reaction mixture was refluxed for 2 h and a solid product was precipitated. A quantity of 3 mmol of the corresponding MCl_2 ($M = Pd^{II}$ and Pt^{II}) was dissolved in hot water for $PdCl_2$ or dilute HCl for $PtCl_2$, and added dropwise to 10 mL of an ethanolic solution of the ligand (6 mmol). The reaction mixture was refluxed for 4 h and a solid product was precipitated. For precipitation of platinum complex the pH of the reaction mixture was adjusted to ≈ 6 using an acetate buffer solution. The solid products were collected by filtration, washed several times with ethanol and allowed for precipitation in air.

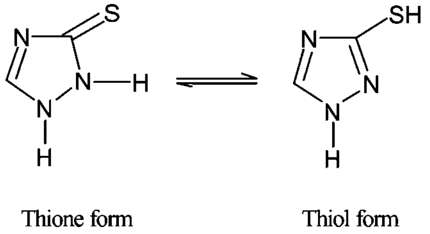
RESULTS AND DISCUSSION

The metal complexation reactions occur according to the following equations

$$MCl_3 + 2H_2TAZ + H_2O \rightarrow M(HTAZ)_2Cl \cdot (H_2O)$$
$$[M = Rh^{III} \text{ and } Ru^{III}]$$
$$MCl_2 + 2H_2TAZ + 2H_2O \rightarrow M(HTAZ)_2(H_2O)_2$$
$$[M = Pd^{II} \text{ and } Pt^{II}]$$

The microanalytical data are shown in Table 1 and are consistent with the formulas $[M(HTAZ)_2Cl{\cdot}(H_2O)]$ ($M = Rh^{III}$ and Ru^{III}), $[M(HTAZ)_2(H_2O)_2]$ and $[M = Pd^{II}$ and $Pt^{II}]$.

1H-1,2,4-triazole-3-thiol (H_2TAZ) has the following tautomeric forms.



Tautomeric Forms of H_2TAZ

The principle IR bands of H_2TAZ and its metal complexes are listed in Table 2.

The H_2TAZ spectrum shows two bands at 3090 and $1653\,cm^{-1}$ assigned to ν(NH) and ν(C=N), respectively. The two strong bands at 1057 and $942\,cm^{-1}$ are assigned to ν(C-N) and ν(N-N), respectively. Also, the ν(C=S) vibrations are observed at 1236 and $705\,cm^{-1}$ with contribution from vibrations, in particular, ν(CN). The spectrum does not display ν(SH) at ca. $2750\,cm^{-1}$ indicating that in the solid state, H_2TAZ remains in the thione form.

The IR spectra of $Rh(HTAZ)_2Cl{\cdot}(H_2O)$ and $Ru(HTAZ)_2Cl{\cdot}(H_2O)$ complexes shows that the H_2TAZ behaves as bidentate coordinating ligand via the azomethine nitrogen and thiol sulphur atom with the replacement of a hydrogen atom from the latter group. This mode of complexation is

Table 1. Analytical and Physical Data of the Investigated Complexes

Compound	Empirical Formula	Formula Weight	Yield %	M.P. (°C)	Color	Found (Calcd.) % C	H	M	Cl
$Rh(HTAZ)_2Cl\cdot(H_2O)$	$C_4H_6ClN_6ORhS_2$	356.62	74	>350	Orange	13.01	2.06	29.15	10.09
		$(350)^a$				(13.47)	(1.69)	(28.85)	(9.94)
$Ru(HTAZ)_2Cl\cdot(H_2O)$	$C_4H_6ClN_6ORuS_2$	354.79	63	>350	Dark-olive	13.92	2.17	28.87	10.31
		$(346)^a$				(13.54)	(1.70)	(28.48)	(9.99)
$Pd(HTAZ)_2(H_2O)_2$	$C_4H_8N_6O_2PdS_2$	342.7	78	Dec.280	Red	14.61	1.91	24.13	–
		$(336)^a$				(14.09)	(2.35)	(24.52)	–
$Pt(HTAZ)_2(H_2O)_2$	$C_4H_8N_6O_2PtS_2$	431.36	71	>350	Brown	11.48	1.42	20.0	–
		$(333)^a$				(11.14)	(1.87)	(19.48)	–

[a] Measured M. Wt.

Table 2. IR Spectroscopic Data of the Investigated Complexes

	IR (cm^{-1})						
Compound	ν(NH)	ν(C=S)	ν(S-C=N)	ν(C-S)	ν(M-N)	ν(M-Cl)	ν(M-Cl)
HTAZ	3090	1236–705	—		—	—	
$Rh(HTAZ)_2Cl\cdot(H_2O)$	3122	—	1620	647	510	439–	281
$Ru(HTAZ)_2Cl\cdot(H_2O)$	3127	—	1625	627	520	425–	320
$Pd(HTAZ)_2(H_2O)_2$	3106	—	1620	637	—	–464	—
$Pt(HTAZ)_2(H_2O)_2$	3112	—	1620	648	—	430	—

supported by the following observations: the disappearance of ν(C=S) with the simultaneous appearance of new bands in range 1620–1625 and 627–647 cm^{-1} assignable to ν(N-N=C) and ν(C-S),[7] respectively. Also, the appearance of three new bands in the range 281–320, 425–439 and 502–510 cm^{-1} assignable to ν(M-Cl), ν(M-S) and ν(M-N),[8] respectively.

On the other hand, the H_2TAZ my acts as monodentate coordinating ligand via the thiol sulphur atom with displacement of a hydrogen atom. This behavior is found in $Pd(HTAZ)_2(H_2O)_2$ and $Pt(HTAZ)_2(H_2O)_2$ complexes. This confirmed by IR spectra, which shows the disappearance of ν(C=S) with the simultaneous appearance of new bands at 1620 and 647 cm^{-1} assignable to ν(S-C=N) and ν(C-S), respectively. Also, the appearance of new band in the range 430–464 assigned to ν(M-S).

The presence of water within the coordination sphere in the hydrated complexes is supported by the observation of bands in the region 3425–3435 and 1630–1660 cm^{-1} in the spectra of the complexes due to OH stretching and HOH deformation. The water of crystallization was determined from the mass loss observed upon heating the complexes in oven at 150°C for three hours.

The ^1H NMR spectrum for the pure ligand H_2TAZ shows three signals at δ 13.40, 8.256 and 8.20 ppm relative to TMS, assigned to the NH, NH and CH protons, respectively.^{13}C NMR spectrum shows two signals at δ 166.04 and 141.072 pmm, which are assigned to the (C=S) and (C=N), respectively. The ^1H NMR spectrum of the Pd^{II} complexes show three signals at δ 8.30, 8.26 and 3.57 ppm relative to TMS, which are assigned to the NH, CH proton and coordinated water, respectively. The Rh^{II}, Ru^{III} and Pt^{II} complexes have paramagnetic properties.

The electronic absorption spectra of the complexes were measured at ambient temperature in 1.22×10^{-3} M to 9.52×10^{-4} M DMSO solutions. The solutions of the complexes exhibit some intraligand transitions in the UV region attributed to π–π^* and n–π^* transitions. The absorption maxima of the π–π^* transition of the investigated complexes are compared to the absorption of the free ligand H_2TAZ which lies at 36,000 cm^{-1} ($\varepsilon = 384$).[9] The absorption bands are red-shifted compared to the free ligand. The spectra of the complexes also show some d–d transitions in the visible region consisting of transitions between different spin-orbital levels. These d–d transitions actually occur and provide evidence for the covalent character of metal-ligand bonds of the investigated complexes.[10]

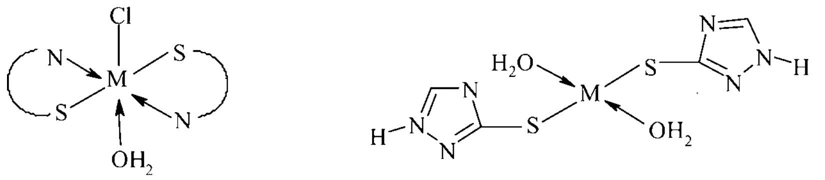
The electronic spectrum of $Rh(HTAZ)_2Cl.(H_2O)$ shows three bands at 23,201, 27,247 and 42,374 cm^{-1} which are referred to $^1T_{1g} \rightarrow {}^1A_{1g}$, $^1T_{2g} \rightarrow {}^1A_{1g}$ and ligand-metal charge transfer,[11] which suggest octahedral structure.

The electronic spectrum of $Ru(HTAZ)_2Cl.(H_2O)$ exhibits two bands at 14,287 and 16,660 cm^{-1} assignable to $^4T_{1g}\rightarrow{}^2T_{2g}$, and $^4T_{2g}\rightarrow{}^2T_{2g}$ transitions[12] in octahedral structure. The ligand-metal charge transfer found at 41,322 cm^{-1}.

The electronic spectrum of $Pd(HTAZ)_2(H_2O)_2$ shows two bands at 32,154 and 37,523 assigned to $^1A_{1g}\rightarrow{}^1B_{1g}$ and $^1A_{1g}\rightarrow{}^1A_{2u}$ transitions in square-planar structure.

The electronic spectrum of $Pt(HTAZ)_2(H_2O)_2$ shows five bands at 19,685, 26,109, 32,415, 37,802 and 40,816 attributed to $^1A_{1g}\rightarrow{}^3A_{1g}$,$^1A_{1g}\rightarrow{}^1A_{2g}$,$^1A_{1g}\rightarrow{}^1B_{1g}$,$^1A_{1g}\rightarrow{}^1A_{2u}$ and $^1A_{1g}\rightarrow{}^1E_u$ transitions,[12] which suggest square-planar geometry for this complex.

Based on the foregoing discussion it may be concluded that 1H-1,2,4-triazole-3-thiol is capable of forming complexes with Rh^{III}, Ru^{III}, Pd^{II} and Pt^{II}. The following general structures of the investigated complexes are plausible.



M=Rh^{III} or Ru^{III} M=Pd^{II} or Pt^{II}

Proposed Structures of the Investigated Complexes

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