

New complexes of 6-Amino-4-hydroxy-2-mercaptopyrimidine

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ABSTRACT

6-Amino-4-hydroxy-2-mercaptopyrimidine (Hahmp) complexes, [Zn(ahmp)₂], *cis*-[Mo₂O₅(ahmp)₂], *cis*-[WO₂(ahmp)₂] and *trans*-[UO₂(ahmp)₂] have been synthesized and characterized on the basis of elemental analysis, thermal and molar conductivity measurements as well as IR, ¹H NMR, and mass spectroscopy. Hahmp acts as a mononegative bidentate, coordinates the metal ions through the deprotonated cyclic nitrogen (N-1) and thione sulfur atom. © 2014 Trade Science Inc. - INDIA

KEYWORDS

Zinc;
Molybdenum;
Tungsten;
Uranyl;
Complexes.

INTRODUCTION

Pyrimidine is an important component of nucleic acids and is used as a building block in pharmaceuticals for the synthesis of antiviral, anticancer, antibacterial and antifungal agents^[1-3]. Recently, our laboratory has been actively involved in the synthesis of various transition metal complexes of 2-thiopyrimidine derivatives^[4-7].

Here we report the synthesis of complexes of 6-amino-4-hydroxy-2-mercaptopyrimidine with Zn(II), Mo(VI), W(VI) and UO₂²⁺. The structures of the complexes are discussed in terms of elemental analyses, spectra (IR, NMR, mass), and thermal and molar conductivity measurements.

EXPERIMENTAL

Materials

All reagents and solvents were purchased from Alfa/Aesar and the manipulations were performed under aerobic conditions using the materials and solvents as

received. DMSO-d₆ was used for the NMR measurements referenced against TMS.

Measurements

Infrared spectra were recorded on a Nicolet 6700 Diamond ATR spectrometer in the 4000- 200 cm⁻¹ range. NMR spectra were recorded on VNMRS 200 and 500 MHz spectrometer in DMSO-d₆ using TMS as reference. Mass spectra were recorded using LCQ Duo and double focusing MS25RFA instruments, respectively. Thermal analyses were made in the 20–800° C range at a heating rate of 20 ° C min⁻¹, using Ni and NiCo as references, on a TA instrument TGA model Q500Analyzer TGA-50. Molar conductivity measurements were carried out at room temperature on a YSI Model 32 conductivity bridge.

Preparations

[Mo₂O₅(ahmp)₂].2H₂O

Aqueous solution of ammonium molybdate, (NH₄)₂[MoO₄] (0.12 g, 0.5 mmol; 10 mL) was added to Hahmp (0.072 g, 0.5 mmol) in ethanol (10 mL). The

Full Paper

reaction mixture was heated under reflux for 7h. The resulting orange solid was filtered off, washed with H₂O and air-dried. Yield: 65%. Anal. Calcd. for C₈H₁₂N₆O₇S₂Mo₂: C, 16.2; H, 2.0; N, 14.2; S, 10.8%. Found: C, 16.4, H, 2.1, N, 14.0; S, 10.9%. Conductivity data (10⁻³ M in DMF): $\Lambda_M = 3.0 \text{ ohm}^{-1}$. IR (cm⁻¹) 3400, 3320, 3229, 1576, 1253, 1193, 928, 899, 547, 437. ¹H NMR (d₆-DMSO/TMS, ppm), δ : 11.70 (s, 1H, O(4)H), 4.60 (s, 1H, C(5)H); 5.62 (s, 2H, NH₂).

[Zn(ahmp)₂].11/3H₂O

Zinc chloride (0.136 g, 1 mmol) in water (2 mL) was added to Hahmp (0.143 g, 1 mmol) in ethanol containing KOH (0.056 g, 1 mmol; 10 mL). The reaction mixture was heated under reflux for 12h, during which an off-white precipitate was obtained. It was filtered off, washed with water, ethanol and air-dried. Yield: 75%. Anal. Calcd. for C₈H_{10.7}N₆O_{3.3}S₂Zn: C, 25.7; H, 2.9; N, 22.5; S, 17.1; Zn, 17.5%. Found: C, 25.8, H, 3.0; N, 22.4; S, 17.2; Zn, 17.6%. Conductivity data (10⁻³ M in DMF): $\Lambda_M = 4.0 \text{ ohm}^{-1}$. IR (cm⁻¹) 3442, 3310, 3233, 1545, 1325, 1273, 1153, 553, 490. ¹H NMR (d₆-DMSO/TMS, ppm), δ : 11.41 (s, 1H, O(4)H); 4.50 (s, 1H, C(5)H); 5.46 (s, 2H, NH₂).

[WO₂(ahmp)₂].H₂O

The synthesis of [WO₂(ahmp)₂] was achieved by a similar procedure to that for [Mo₂O₅(ahmp)₂] with Na₂[WO₄] replacing (NH₄)₂[MoO₄]. Yield: 59%. Anal. Calcd. for C₈H₁₀N₆O₅S₂W: C, 18.5; H, 1.9; N, 16.2; S, 12.4%. Found: C, 18.6, H, 2.0, N, 16.0; S, 12.2%. Conductivity data (10⁻³ M in DMF): $\Lambda_M = 2.0 \text{ ohm}^{-1}$. IR (cm⁻¹) 3405, 3321, 3234, 1575, 1254, 1191, 934, 898, 437. ¹H NMR (d₆-DMSO/TMS, ppm), δ : 11.68 (s, 1H, O(4)H), 4.54 (s, 1H, C(5)H); 5.58 (s, 2H, NH₂).

[UO₂(ahmp)₂]

A stirred solution of uranyl nitrate (0.26 g, 0.5 mmol) in MeOH (5 mL) was added to a solution of Hahmp (0.072 g, 0.5 mmol) in MeOH (15 mL). The reaction mixture was stirred and heated under reflux in a steam-bath for 6h, during which an orange precipitate was isolated. It was filtered off, washed with hot MeOH, Et₂O and air-dried. Yield: 55%. Anal. Calcd. for C₈H₈N₆O₄S₂U: C, 17.3; H, 1.4; N, 15.2; S, 11.6%. Found: C, 17.5, H, 1.3, N, 15.3; S, 11.5%. Conduc-

tivity data (10⁻³ M in DMF): $\Lambda_M = 8.0 \text{ ohm}^{-1}$. IR (cm⁻¹) 3408, 3320, 3237, 1578, 1257, 1190, 972. ¹H NMR (d₆-DMSO/TMS, ppm), δ : 11.69 (s, 1H, O(4)H), 4.51 (s, 1H, C(5)H); 5.56 (s, 2H, NH₂). ESI-MS (*m/z*): 555 [UO₂(ahmp)₂]⁺, 413 [UO₂(ahmp)]⁺.

RESULTS AND DISCUSSION

The experimental section describes the synthesis of some new complexes of 6-amino-4-hydroxy-2-mercaptopyrimidine (Hahmp). The elemental analyses of the complexes are in agreement with the assigned formulae. The molar conductivities (Λ_M) in DMF at room temperature suggest all complexes to be non-electrolytes^[6-8].

Vibration spectra

The characteristic IR bands and vibrational assignments for 6-amino-4-hydroxy-2-thiopyrimidine (Hahmp) were reported earlier^[7]. The IR spectrum of Hahmp shows bands at 3407 and 3313 cm⁻¹ due to $\nu_{as}(\text{NH}_2)$ and $\nu_s(\text{NH}_2)$ stretching vibrations, respectively, while the strong band at 3215 cm⁻¹ is associated with the $\nu(\text{OH})$ stretching vibration^[6,7,9]. The presence of the $\nu(\text{NH})$ stretch at 2904 cm⁻¹^[10], the absence of the $\nu(\text{SH})$ mode near 2600 cm⁻¹ and the presence of the characteristic thioamide bands due to extensive coupling of $\delta(\text{NH})$, $\nu(\text{C}=\text{N})$, $\nu(\text{NCS})$, and $\nu(\text{C}=\text{S})$ modes at 1634, 1585, and (1383, 1271, 1180) cm⁻¹, respectively, support the existence of Hahmp in the thione form (Figure 1)^[5-7,11,12].

In complexes, Hahmp acts as a mononegative bidentate ligand, coordinating the metal ions through the thione sulfur and the deprotonated cyclic nitrogen (N-1) atoms^[6,7,13]. This mode of chelation is supported by the shift observed in the $\nu(\text{C}=\text{S})$ and $\nu(\text{N}=\text{C}=\text{S})$ as

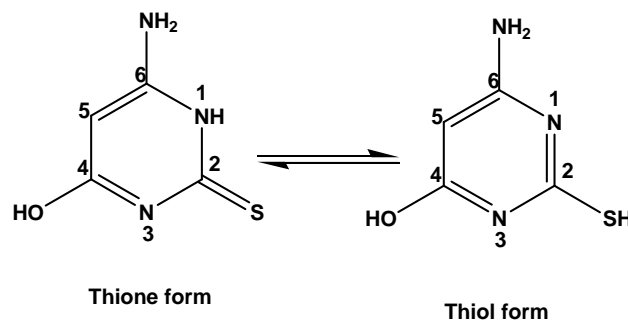


Figure 1 : Thione-thiol form of 6-amino-4-hydroxy-2-mercaptopyrimidine (Hahmp)

well as the absence of the $\nu(\text{NH})$ and $\delta(\text{NH})$ stretches^[7]. The $\nu_s(\text{NH}_2)$, $\nu_{as}(\text{NH}_2)$, and $\nu(\text{OH})$ stretches observed more or less in the same position as in the free Hahmp^[7,14]. These observations indicate the replacement of the acidic hydrogen by the metal ion, forming four-membered chelate ring^[6,7]. The same mode of chelation has early been reported in X-ray crystallographic studies^[13,15]. Also, the same feature has been noted in 6-amino-4-hydroxy-2-thiopyrimidine (Hahtp) complexes, $[\text{Zn}(\text{ahtp})_2(\text{H}_2\text{O})_2]$, $[\text{Zn}(\text{ahtp})_2(\text{PPh}_3)(\text{H}_2\text{O})]$, $[\text{Ag}(\text{ahtp})(\text{H}_2\text{O})_2]$, $[\text{Ag}(\text{ahtp})(\text{PPh}_3)(\text{H}_2\text{O})]$ and $[\text{Ag}(\text{ahtp})\text{L}]$ (L = bpy, phen)^[7].

In the 1000–750 cm^{-1} region, the spectrum of $[\text{Mo}_2\text{O}_5(\text{ahmp})_2]$ (Figure 2) exhibits bands characteristic of *cis*- MoO_2^{2+} units and $\{\text{O}_2\text{Mo}-\text{O}-\text{MoO}_2\}^{2+}$ ^[16]. The IR bands at 928 and 899 cm^{-1} are assigned to the $\nu_s(\text{MoO}_2)$ and $\nu_{as}(\text{MoO}_2)$ modes, respectively^[16]. As expected, the symmetric mode is weak in the IR spectra, while the opposite applies for the antisymmetric mode. The appearance of two stretching bands is indicative of the *cis* configuration^[17]. The strong IR band at 745 cm^{-1} is assigned to the $\nu_{as}(\text{Mo}-\text{O}-\text{Mo})$ mode^[18], indicating the presence of a $(\mu\text{-O})^2$ group. For the complex, $[\text{WO}_2(\text{ahmp})_2]$, the $\nu_s(\text{WO}_2)$ and $\nu_{as}(\text{WO}_2)$ bands appear near 930 and 900 cm^{-1} , respectively. The $\nu_s(\text{WO}_2)$ and $\nu_{as}(\text{WO}_2)$ modes are observed at higher wavenumbers when compared to those of the analogous Mo(VI) derivative, suggesting that the *cis*- WO_2^{2+} moiety has some “triple” bond character^[5,18]. The IR spectrum of *trans*- $[\text{UO}_2(\text{ahmp})_2]$, exhibits only one U=O stretching band, $\nu_{as}(\text{UO}_2)$, at 972 cm^{-1} indicating its linear *trans*dioxo configuration^[5,17]. The spectra of the complexes show several bands near 420 and 350 cm^{-1} due to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{S})$ stretches, respec-

tively^[5-7].

¹H NMR spectra

The ¹H-NMR data for the free Hahmp ligand and some of its complexes in DMSO-*d*₆ are given in the experimental section. As we have reported earlier, the ¹H NMR spectrum of Hahmp shows four singlets at δ 4.68, 5.66, 6.34 and 11.80 ppm arising from H(5), NH₂(6), NH(1) and OH(4), respectively (see Figure 1 for numbering scheme)^[7].

In the ¹H-NMR spectra of the complexes, the NH(1) singlet is not observed, while that of NH₂ shows an upfield shift confirming the coordination of ahmp through the thione sulfur and deprotonated cyclic (N-1) centers^[7].

Mass spectra

The mass spectra of the complexes are reported in the Experimental section and their molecular ion peaks are in agreement with their assigned formulae. The mass spectrum of $[\text{Zn}(\text{ahmp})_2]$ shows fragmentation patterns corresponding to the successive degradation of the complex. The first peak at m/z 700.0 with 39 % abundance represents the molecular ion $[\text{Zn}(\text{ahmp})_2]^+$ (Calcd. 699.0). The peaks at 414.9 (Calcd. 415.0), 349.3 (Calcd. 349.5) and 207.5 (Calcd. 207.5) corresponding to $[\text{Zn}_2(\text{ahmp})_2]^+$, $[\text{Zn}(\text{ahmp})_2]^+$ and $[\text{Zn}(\text{ahmp})]^+$ fragments, respectively^[7]. The mass spectra of the complexes, $[\text{Mo}_2\text{O}_5(\text{ahmp})_2]$, $[\text{WO}_2(\text{ahmp})_2]$ and $[\text{UO}_2(\text{ahmp})_2]$ exhibit signals at m/z 556.0 (Calcd. 555.9), 499.9 (Calcd. 499.0) and 555 (Calcd. 554) with 21.9, 15.0 and 11% abundance corresponding to $[\text{Mo}_2\text{O}_5(\text{ahmp})_2]^+$, $[\text{WO}_2(\text{ahmp})_2]^+$ and $[\text{UO}_2(\text{ahmp})_2]^+$ fragments, respectively. A step-wise ligand loss show signals at 414 (Calcd.313.9), 357.9 (Calcd. 357.0) and

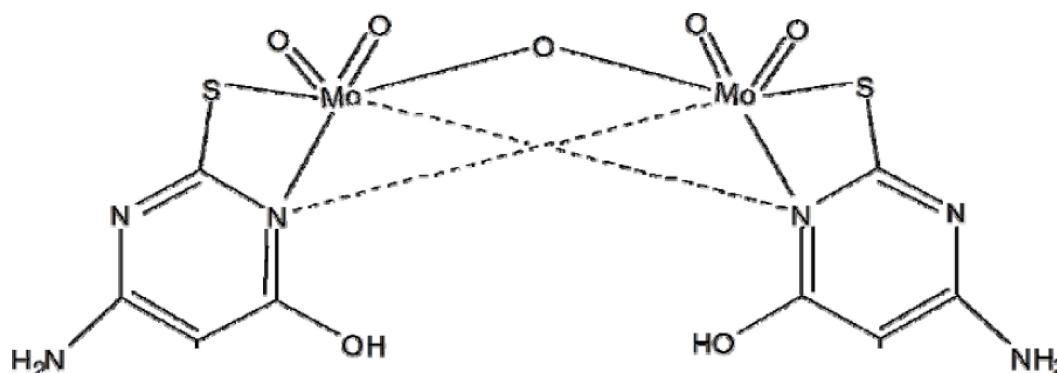


Figure 2 : Structure of $[\text{Mo}_2\text{O}_5(\text{ahmp})_2]$

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413.0 (Calcd. 412) corresponding to $[\text{Mo}_2\text{O}_5(\text{ahmp})]^+$, $[\text{WO}_2(\text{ahmp})]^+$ and $[\text{UO}_2(\text{ahmp})]^+$ fragments, respectively.

Thermal measurements

The thermal stability and degradation behaviour of $[\text{Zn}(\text{Hahmp})_2].4/3\text{H}_2\text{O}$ and $[\text{Mo}_2\text{O}_5(\text{ahmp})_2].2\text{H}_2\text{O}$, were studied using the thermogravimetric (TG) technique. The weight loss observed below 130°C is due to dehydration as the colours changed from pale to deeper^[19].

The thermogram of *cis*- $[\text{Mo}_2\text{O}_5(\text{ahmp})_2].2\text{H}_2\text{O}$ shows the first-step weight loss of 6.3% between 46 and 145°C , corresponds almost exactly to the release of two waters per molecule of complex (Calcd. 6.1%); the relatively low temperature shows that these water molecules are crystal lattice held^[4]. Another endothermic decomposition occurs between 261 and 401°C , attributed to the loss of $\text{C}_3\text{H}_4\text{N}_2\text{O}$ and $\text{C}_3\text{H}_4\text{N}_2$ fragments (Calcd. 25.7, Found 25.5%)^[6,7]. There is one more TG inflection between $402 - 539^\circ\text{C}$, which may arise from the elimination of two NCS fragments (Calcd. 19.6, Found 19.9%), leaving MoO_3 (48.6%).

The thermogram of $[\text{Zn}(\text{ahmp})_2].4/3\text{H}_2\text{O}$ shows five TG inflections in the 45 – 169, 170 - 248, 249 - 376, 377 - 498 and 499 - 685°C regions. These weight losses are arising from the release of hydrate water (Calcd. 6.4, Found 6.7%), H_2 and $\frac{1}{4}\text{N}_2$ (Calcd. 2.4, Found 2.3%), C_3HNO (Calcd. 17.9, Found 18.2%), NCSN (Calcd. 19.3, Found 19.5%), $\text{C}_3\text{H}_3\text{N}_2$ (Calcd. 17.9, Found 18.0%) fragments, respectively, leaving residue of ZnO (21.8%).

CONCLUSIONS

New complexes of Hahmp have been prepared and characterized. The Hahmp ligand shows mononegative bidentate, through thione sulfur and deprotonated cyclic nitrogen (N-1) centers.

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