# Ruthenium(III) and Ruthenium(II) Complexes with 6-Mercaptopurine

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## Abstract

Complexes of ruthenium(II) and (III) with 6-mercaptopurine have been prepared by refluxing ethanolic solutions of the metal chloride with 6-mercaptopurine. Complexes of the type Ru(6-MP)$Cl_3 \cdot 2H_2O$, Ru(6-MP)$_2Cl_3 \cdot 6H_2O$, Ru(6-MP)$_2$(DMSO)$_3Cl_2 \cdot H_2O$ and Ru(6-MP)$_4Cl_2 \cdot 2H_2O$ were isolated from the reaction mixture. The compounds prepared were characterized by elemental analysis, infrared, electronic, $^1H$ NMR spectroscopy, and conductivity measurements. The physical and chemical methods supported evidence that in the ruthenium(III) complexes 6-mercaptopurine behaves as a chelating ligand binding to the metal through N(7) and S(6) while in the ruthenium(II) complexes the ligand is binding to the metal through N(7).

## Introduction

Synthesis of platinum group metal complexes of nucleic acid bases and their derivatives have acquired an interest recently due to their antitumor and antibacterial activity [1–6]. Since the discovery by Rosenberg [3–5] that platinum ammines are effective as anticancer drugs has provoked the search for similar antitumor agents based on platinum and other transition metals. Many of these drugs appear to interfere with the replication of DNA by binding directly to the cellular DNA [7]. Antitumor-active platinum compounds like *cis*-[Pt$(NH_3)_2Cl_2$] may form intrastrand cross-links in DNA [8–10]. This seems to be a key step in its mechanism of action [11–12]. Also an octahedral complex of Ru(II) *cis*-[Ru$(H_2O)_2(NH_3)_4$] interacts with DNA and has been shown to have biological activity comparable to that of the platinum species [13]. Since the platinum drugs in use at the present time, are not selective for tumor cells exhibit a number of undesirable side effects. It is hoped that by using other metal ions and giving careful attention to their chemical properties more selective and less toxic agents can be developed.

The octahedral complex of Ru(II) *cis*-[Ru(DMSO)$_4Cl_2$] interacts with DNA and has been shown to have biological activity similar to that of the platinum species [13]. Also several ruthenium ammine complexes have been shown to inhibit DNA synthesis *in vitro* at a level similar to that of *cis*-[$Cl_2(NH_3)_2$Pt] [13, 14] and have also shown antitumor activity in animal studies. Pentaammineruthenium(II) and (III) bind to DNA [15] and their complexes with nucleic acid bases and their derivatives have been extensively studied [16–20]. The aquopentaammineruthenium(II) ion shows a unique selectivity for heterocyclic nitrogen bases and a number of purine complexes bound to the metal through the N(7) site have been prepared [16, 19]. Purine ligands can also bind to the metal ion through the carbon adjacent to the nitrogens on the imidazole ring [19] in a manner analogous to the series of ruthenium–imidazolylidene compounds synthesized by Sunberg [27]. Some ruthenium(II) and (III) complexes with various nucleic acid bases, nucleosides and ATP have been prepared and characterized [28–31].

Though work on platinum(II) complexes with 6-mercaptopurine have been reported [32, 33] the respective complexes of ruthenium(III) and ruthenium(II) have not been investigated. The present work has been undertaken to study the interaction of octahedral ruthenium(III) and (II) with 6-mercaptopurine.

## Experimental

### *Materials*

6-Mercaptopurine was obtained from Sigma Chemical Company and used without further purification. $RuCl_3 \cdot 3H_2O$ was from Johnson Mathey Co. and Ru(DMSO)$_4Cl_2$ was prepared according to literature methods [34].

### *Preparation*

$RuCl_3 \cdot 3H_2O$ (1 mmol) was added to a suspension of 6-mercaptopurine (1 mmol) or 2 mmol) in

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methanol. The mixture was refluxed for 3 h and then filtered. The filtrate upon refrigeration precipitated the respective complexes. They were filtered, washed with methanol and dried *in vacuo* over $P_2O_5 \cdot RuCl_2(DMSO)_4$ prepared according to literature methods [34] and 1 mmol was added to a suspension of 6-mercaptopurine (2 or 4 mmol) in ethanol (1:2 and 1:4 mol-ratio respectively). The mixture was then refluxed for 3 h and filtered. During that time the solution became clear and developed a dark green color, indicating a reaction was taking place and the presence of Ru(II) [34]. On standing upon refrigeration the respective 1:2 and 1:4 metal to ligand complexes precipitated. They were filtered, washed repeatedly with water and dried *in vacuo* over $P_2O_5$.

*Physical Methods*

The $^1H$ NMR spectra were measured in DMSO-$d_6$ using an XL-100-15NMR spectrometer. The chemical shifts are related to TMS as internal standard at ambient temperatures.

Conductivity measurements were carried out in DMSO, water and DMF at 25 °C by means of an E365B conductoscope, Metrohm Ltd, Herisau, Switzerland. $\Delta m$ values are expressed in $ohm^{-1}$ $cm^{-1}$ $mol^{-1}$. Infrared spectra were obtained on KBr pellets on a Perkin Elmer Grating Infrared Spectrometer, Model 283.

Diffuse reflectance spectra were recorded on a Varian 634 Model at room temperature. Magnetic susceptibilities were measured at room temperature, by the Faraday method using a Cahn R.G. Electrobalance, PAR Model 155, using $HgCO(NCS)_4$ as a standard.

## Results and Discussion

The elemental analyses and other physical properties of the prepared complexes are listed in Table I. The compounds were not very soluble in common organic solvents however their solubilities in $H_2O$ and DMSO allowed NMR and conductivity measurements. Molar conductance values indicate that the ruthenium(III) complexes are weak electrolytes. $Ru(6MP)_2(DMSO)_3Cl_2 \cdot H_2O$ behaves as a 1:2 electrolyte, while $Ru(6\text{-}MP)_4Cl_2 \cdot 2H_2O$ decomposes in these solvents. The conductivity measurements were taken immediately after preparation of the solutions since it was observed that they change with time indicating replacement of the ligands by the solvent.

The infrared spectra of the compounds are listed in Table II. The band around 3100 $cm^{-1}$ is assigned to the presence of weak $NH^+ \cdots Cl$ intermolecular hydrogen bonding of the ring protonated N(1) atom and a chlorine atom of another complex molecule. This is in agreement with mono and di-substituted purine derivatives [35–37] where the existence of strong hydrogen bonds give rise to intense absorptions near 2400 $cm^{-1}$ while weak hydrogen bonding obtained by replacement of $Cl^-$ with $ClO_4^-$ gave the same aborption at 3200 $cm^{-1}$. Thiols absorb near 2400 $cm^{-1}$ [38]. This band does not appear either in the spectra of the pure ligand or in the spectra of the complexes indicating that 6-mercaptopurine and the complexes exist in their thione form.

When protonation of complexation occurs on the nitrogen of the purine ring the C=C and the C=N stretching vibrations increase in frequency [35–37]. This band which, in the pure ligand appears at 1600 $cm^{-1}$, in the complexes increases in frequency and is observed around 1635 $cm^{-1}$ thus indicating complexation through the N(7) of the imidazole ring. This increase in energy indicates the non-availability of the lone pair of electrons on the nitrogen atom to participate in the ring resonance since they are donated to the metal to form a bond. Thus the C=N bond acquires a more localized double bond character and its frequency increases by 40 $cm^{-1}$. A further increase in the C=N stretching

TABLE I. Analytical Data for Ruthenium–6 mercaptopurine Complexes.

| Complex | Colour | Dec. T (°C) | % Found (Calcd) | | | | $\mu_{eff}$ | $\Lambda_M$ |
|---|---|---|---|---|---|---|---|---|
| | | | C | H | N | Cl | | |
| | | | | | | | (BM) | $cm^2$ $ohm^{-1}$ $mol^{-1}$ c: $1 \times 10^{-3}$ M at 25 °C |
| $Ru(6\text{-}MP)Cl_3(Il_2O)_2$ | black | 292 | 15.79 (15.18) | 1.97 (2.02) | 14.31 (14.37) | 26.54 (26.89) | 1.41 | 10.24(22.58)[a] in DMSO |
| $Ru(6\text{-}MP)_2Cl_3(H_2O)_6$ | brown | 150 | 19.71 (19.36) | 3.32 (3.23) | 17.96 (18.07) | 17.54 (17.16) | 1.55 | 13.21(17.04)[a] in DMSO |
| $Ru(6\text{-}MP)_2(DMSO)_3Cl_2(H_2O)$ | brown | 116 | 25.87 (25.73) | 3.46 (3.48) | 14.50 (15.00) | 9.56 (9.50) | diam. | 229.41(295.41)[a] in $H_2O$ |
| $Ru(6\text{-}MP)_4Cl_2(H_2O)_2$ | yellowish | 146 | 29.33 (29.39) | 2.81 (2.94) | 27.31 (27.43) | 8.74 (8.68) | diam. | 145.77 (dec. in $H_2O$) |

[a]After 72 hours.

TABLE II. Infrared Data of Ruthenium–6 Mercaptopurine and Related Complexes ($cm^{-1}$).

| Band Assign. | 6-MP | Cu(I)–(6-MP) | Hg(II)–(6-MP) | Ru(III)–(6-MP) (1:1) | Ru(III)–(6-MP) (1:2) | Ru(II)–(6-MP) (1:2) | Ru(II)–(6-MP) (1:4) |
|---|---|---|---|---|---|---|---|
| $\nu_{purine}$ ring···· | 1605s | 1620s | 1600s | 1640s | 1640s | 1635s | 1630s |
| ring···· | 1570s | 1580s | 1580s | 1590m | 1580m | 1575m | 1575m |
| | 1520s | 1520s | 1515s | | | | |
| | 1400 | 1390m | 1395m | 1390m | 1420m | 1420m | 1400s |
| | 1345s | 1340m | 1340s | 1345m | 1340m | 1345s | 1350w |
| | 1275m | 1275w | 1270w | | | 1290w | 1290w |
| $\beta_{NH}$···· | 1220s | 1220m | 1220m | 1220m | 1230m | 1230m | 1235m |
| $\nu_{C=S}$··· | 1150s | | | | | 1165m | 1165m |

frequency is expected upon protonation of the purine ring as has been observed in the protonated forms of adenosine, cytidene and other purine derivatives [39].

It has been observed for a number of thione ligands that in coordination through the sulfur, the C=S stretching vibration decreases dramatically in intensity and in most cases completely disappears [32, 33, 38, 41]. In the infrared spectra of platinum-(II) complexes with 6-mercaptopurine riboside, for example [32, 33], the band at 1170 $cm^{-1}$ disappears due to the C=S stretching vibration of the free ligand. In the spectra of the structurally known complexes $Cu(I)(6\text{-MPH})Cl_2 \cdot H_2O$ and $Hg(II)(6\text{-MP})_2Cl_2$ [42] where the metal ions coordinated through the sulfur, the band at 1150 $cm^{-1}$ is absent. However in the infrared spectra of $Ru(II)(6\text{-MP})_4Cl_2 \cdot H_2O$ the band at 1150 $cm^{-1}$ is present suggesting very strongly that Ru(II) is not coordinated through the sulfur. In the complexes $Ru(III)(6\text{-MP})Cl_3 \cdot 2H_2O$ and $Ru(III)(6\text{-MP})_2Cl_3 \cdot 6H_2O$ the absence of the band at 1150 $cm^{-1}$ indicates that ruthenium(III) is coordinated to 6-mercaptopurine through the sulfur. Thus in the ruthenium(III) complexes the absence of the band around 1150 $cm^{-1}$ and the increase in frequency of the absorption band around 1600 $cm^{-1}$ by more than 30 $cm^{-1}$ suggests that in the ruthenium(III) compounds, 6-mercaptopurine is chelated through the N(7) and the S(6). Similar effects have also been observed with complexes where 6-mercaptopurine behaves as a chelated ligand [32, 33, 41].

Infrared spectroscopy has been widely used to distinguish between oxygen- and sulfur-bonded sulfoxide ligands. In the free uncoordinated DMSO the S=O band appears at 1055 $cm^{-1}$. In the complexes, donation via oxygen causes a shift of $\nu$(SO) to lower wave numbers (1000–900) $cm^{-1}$, while S-bonding generally causes an increase of $\nu$(SO) to above 1100 $cm^{-1}$ [43, 44]. In the infrared spectrum of Ru(II) $(6\text{-MP})_2(DMSO)_3H_2O$ the presence of absorption bands at 1080 and 980 $cm^{-1}$ suggests that oxygen-bonded and sulfur-bonded DMSO molecules exist.

The metal–sulfur stretching vibrations appear in the region 500–400 $cm^{-1}$ [45] and the presence of characteristic bands in this area for the Ru(III) complexes strongly suggests the proposed structures, while the absence of bands in that area for the $Ru(II)(6\text{-MP})_4Cl_2 \cdot 2H_2O$ indicate that Ru(II) coordinates through the nitrogen of the ligand. The metal chlorine stretching modes that appear in the region 300–350 $cm^{-1}$ are weak and broad and no definite conclusions can be drawn concerning their stereochemistry. However, the presence of only one metal–chlorine stretching mode around 310 $cm^{-1}$ indicates that the ruthenium-complexes except $Ru(6\text{-MP})Cl_3 \cdot 2H_2O$ exist in their *trans* configuration. The $Ru(6\text{-MP})Cl_3 \cdot 2H_2O$ complex exhibits three bands in that area and most probably occupies *cis* configuration. Furthermore, from the position and the shape of the metal–halogen vibrations evidently there are no bridging configurations of the complexes through Cl···M···Cl bonds. NMR studies on the Ru(II) complexes in DMSO confirm that N(7) is involved in coordination (Table III). Protons attached to the carbon atoms that are closest to the bonding site are known to shift more downfield than others [46, 47]. It has been reported for several nucleic acid derivatives upon complexation that the shift displace-

TABLE III. Proton Chemical Shifts of Free and Coordinated 6-Mercaptopurine in $d_6$-DMSO.

| Complex | C(8)H | C(2)H |
|---|---|---|
| 6-MP | 8.16 | 8.35 |
| Ru(II)–(6-MP) (1:2) | 9.76 | 9.76 |
| Ru(II)–(6-MP) (1:4) | 8.90 | 8.63 |

TABLE IV. Diffuse Reflectance, Electronic Spectra of Ruthenium–6-Mercaptopurine Complexes.

| Complex | $\lambda_{max}$ (nm) | Assignment | $10Dq$ ($cm^{-1}$) | $B$ ($cm^{-1}$) | $C$ ($cm^{-1}$) |
|---|---|---|---|---|---|
| Ru(III)–(6-MP) (1:1) | 658 | $^4T_{1g} \leftarrow {}^2T_{2g}$ | 19796 | 219 | 876 |
| | 590 | $^4T_{2g} \leftarrow {}^2T_{2g}$ | 19796 | 219 | 876 |
| | 430 | $^2A_{2g}, {}^2T_{1g} \leftarrow {}^2T_{2g}$ | | | |
| Ru(III)–(6-MP) (1:2) | 636 | $^4T_{1g} \leftarrow {}^2T_{2g}$ | | | |
| | 580 | $^4T_{2g} \leftarrow {}^2T_{2g}$ | 19713 | 190 | 760 |
| | 400 | $^2A_{2g}, {}^2T_{1g} \leftarrow {}^2T_{2g}$ | | | |
| Ru(II)–(6-MP) (1:2) | 630 | $^3T_{1g} \leftarrow {}^1A_{1g}$ | | | |
| | 530 | $^3T_{2g} \leftarrow {}^1A_{1g}$ | 29564 | 375 | 4564 |
| | 400 | $^1T_{1g} \leftarrow {}^1A_{1g}$ | | | |
| Ru(II)–(6-MP) (1:4) | 635 | $^3T_{1g} \leftarrow {}^1A_{1g}$ | | | |
| | 490 | $^3T_{2g} \leftarrow {}^1A_{1g}$ | 21029 | 1904 | 5284 |
| | 380 | $^1T_{1g} \leftarrow {}^1A_{1g}$ | | | |
| | 350 | C.T. | | | |

ment of H(8) by 0.6–0.8 ppm has been ascribed to metal binding via N(7). Thus the largest shift change occurs with the H(8) proton next to the coordination site, giving a shielding order H(2) > H(8). This order is reversed to that observed for the free ligand and has been found when protonation or alkylation is directed to the imidazole ring [40]. In $W(CO)_5$(6-MP) [41] and the structurally known $HgCl_2$(6-MP) [42] where the heterocyclic ligand is coordinated via S(6) their NMR spectra in DMSO exhibit ~0.5 ppm downfield shift of H(2) relative to H(8).

In conclusion, the NMR spectra of the ruthenium-(II) complexes support the evidence that 6-mercaptopurine behaves as a monodentate ligand binding to the metal through the N(7).

Solid state electronic spectra confirm an octahedral configuration for ruthenium(III) and ruthenium(II) complexes. The position of the electronic absorption bands and their electronic assignments are given in Table IV. The ground state for ruthenium(III) complexes is $t_{2g}^5$ [47] with only one unpaired electron. As expected for a $d^5$ configuration the electronic spectra show a complex structure since many d–d transitions are expected from the $^2T_{2g}$ ground state. The strong field electrostatic matrices of Tanabe and Sugano [48] predict eight transitions from the $t_{2g}^5$ ground state to the doublet $t_{2g}^4 e_g^1$ configuration and two transitions from the ground state to the $t_{2g}^4 e_g^1$ quartet states. In the strong crystal field the five electrons will all go into the lower $t_{2g}$ level not quite filling it up. Therefore, both the lower $t_{2g}$ level and the higher $e_g$ level may act as acceptor level. In the spectra of the ruthenium(III) complexes, six maxima are present. The low intensity of these transitions suggests that they are crystal field transitions and they appear to be characteristic of octahedral complexes of ruthenium-(III) [47–49]. From the values of spectroscopic terms in Table IV we have calculated the parameters $10\,Dq$, $B$ and $C$, using the transitions:

$$^4T_{1g} \leftarrow {}^2T_{2g} \qquad 10Dq - 5B - 4C$$

$$^4T_{2g} \leftarrow {}^2T_{2g} \qquad 10Dq + 3B - 4C$$

$$^2A_{2g}, {}^2T_{1g} \leftarrow {}^2T_{2g} \qquad 10Dq - 2B - C$$

and assuming $C/B = 4$ [48].

The ground state for Ru(II) is $t_{2g}^6$ the respective spectroscopic term $^1A_{1g}$ and for the excited state $t_{2g}^5 e_g^1$ corresponds to the following spectroscopic terms in order of increasing energy $^3T_{1g}$, $^3T_{2g}$, $^1T_{2g}$ and $^1T_{2g}$ [51]. From the transitions [52]:

$$^3T_{1g} \leftarrow {}^1A_{1g} \qquad 10Dq - 3C$$

$$^3T_{2g} \leftarrow {}^1A_{1g} \qquad 10Dq + 8B - 3C$$

$$^1T_{2g} \leftarrow {}^1A_{1g} \qquad 10Dq - C$$

$$^1T_{2g} \leftarrow {}^1A_{1g} \qquad 10Dq + 16B - C$$

we have calculated the values $10Dq$, $B$ and $C$ for the Ru(II) complexes. From the values of these parameters and the positions of the bands it becomes evident that the Ru(II) complexes are octahedral [53].

The considerable decrease in the value of the Racah interelectronic repulsion parameter $B$ from that of the free ions [52] along with the increased value observed for $Dq$ suggest that covalent bonding

occurs between the ligand and the central atom in the complexes. Thus spectroscopic data suggests that in the ruthenium(III) complexes 6-mercaptopurine behaves as a chelating ligand binding to the metal through the N(7) and S(6), while in the ruthenium-(II) complexes 6-mercaptopurine is binding to the metal through N(7). Taking into consideration their insolubilities in common organic solvents polymeric structures cannot be excluded.

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