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# Synthesis and Characterization of Some Ruthenium(III) Complexes of Semicarbazones Derived from 4-Aminoantipyrine

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In the present work, we describe a new series of ten ruthenium(III) complexes of semicarbazones derived from 4-aminoantipyrine and varions aryl aldehydes. The complexes have the general composition [Ru(L)$Cl_3$]. All the complexes were characterized by chemical analysis, conductance, magnetic moment measurements, infrared and electronic spectra. The ligands behave as neutral tridentate (N,N,O) molecules. The complexes are six-coordinated octahedral.

## INTRODUCTION

Interest in the interaction of platinum metals with biologically important molecules began about 30 years ago when Rosenberg *et al.*[1] published their discovery that certain platinum complexes exhibit anticancer activity. When considering the biochemistry of ruthenium complexes, it is important to examine their major binding sites with nucleic acids. The study of Ru(II) and Ru(III) binding to nucleic acids was begun before it was widely known that the activity of the platinum anticancer drugs was probably dependent on nucleic acid binding. The primary object of the investigation was to examine novel models of metal-purine coordination, particularly carbenoid binding.[2, 3] Because of their oxidation states, the pentamine ruthenum(II & III) ions were studied.[4, 5] The results showed that Ru(II) has similar coordination to that shown by the platinum anticancer drugs so that analogous effects might be exerted on nucleic acid metabolism. For example, the attachment at the N(7) of deoxyguanosine has been shown to occur for both amine ruthenium(II & III) ions. Amine ruthenium(III) species, however, form unusual cystosinato and adenosinato species *via* coordination to the oxocyclic nitrogen[6, 7]. A high percentage of the compounds tested, which would be expected to function as Ru(III) prodrugs, have exhibited antitumour activity. *fac*-[$RuCl_3(NH_3)_2$] was shown to cause 100% elongation of filament of *E. coli* during testing of a series of chloro-ammine Ru complexes, and it has subsequently been shown to be as good as cisplatin towards P-388 leukaemia. A ruthenium complex which is even more active than this against this leukaemia screen has been made by replacing ammonia and imidazole [$RuCl_4(Im)_2$]ImH. In view of the above, in the present work, we describe the synthesis and characterization of some six-coordinated ruthenium(III) coordination compounds derived from semicarbazones of 4-aminoantipyrine, *viz*., 4[N-(4-benzalidene) amino] antipyrine semicarbazone (BAAPS), 4[N-(2-hydroxybenzalidene) amino] antipyrine semicarbazone. (HBAAPS), 4[N-(4-methoxybenzalidene) amino] antipyrine semicarbazone (MBAAPS), 4[N-(4-dimethylaminobenzalidene) amino] antipyrine semicarbazone (DABAAPS), 4[N-(2′-nitrobenzalidene) amino] antipyrine semicarbazone (2′-$NO_2$BAAPS), 4[N-(3′-mitrobenzalidene) amino] antipyrine semicarbazone (3′-$NO_2$BAAPS), 4[N-(4′-nitrobenzalidene) amino] antipyrine semicarbazone (4′-$NO_2$BAAPS), 4[N-(4-hydroxy-3-methoxybenzalidene) amino] antipyrine semicarbazone (HMBAAPS), 4[N-(2-hydroxy-1-naphthalidene) amino] antipyrine semicarbazone (HNAAPS) and 4[N-(cinnamalidene) amino] antipyrine semicarbazone (CAAPS).

## EXPERIMENTAL

All the chemicals used are of AnalaR grade. All the ten semicarbazones of 4-aminoantipyrine were synthesized as reported elsewhere.[8, 9]

All the complexes were synthesized by the following general method. Hot ethanolic solution of the ruthenium(III) chloride (0.001 mol) was mixed with hot ethanolic solution of the respective semicarbazone (0.001 mol). The reaction mixture was refluxed for *ca*. 3–4 h. The contents were cooled and after reducing the volume of the solution to half; it led to precipitation of the desired complexes. The complexes were filtered, washed with hot ethanol and dried in an oven at 110°C.

All the physical measurements and analyses were performed as reported earlier[8, 10].

## RESULTS AND DISCUSSION

The reaction of ruthenium(III) chloride with BAAPS, HBAAPS, MBAAPS, DABAAPS, 2′-$NO_2$BAAPS, 3′-$NO_2$BAAPS, 4′-$NO_2$BAAPS, HMBAAPS, HNAAPS and CAAPS gave complexes of the general composition $Ru(L)Cl_3$. All the complexes gave satisfactory elemental analyses results (Table-1). All the complexes are quite stable and can be stored for months without any appreciable change. The molar conductance values of the complexes are too low to account for any dissociation; therefore, we consider that all these complexes are non-electrolytes. Ruthenium(III) belongs to the $d^5$ system and as such has five electrons in the outer orbital. The $Ru^{3+}$ complexes show magnetic moments of 1.84–1.90 B.M. at room temperature, which are lower than the spin only value. The lowering of $\mu_{eff}$ values may arise due to effect of ligand-field, metal-metal interaction or considerable delocalization. These values ruled out the possibility of square-planar or square-bipyramidal type of complexes. The only possible stereochemistry concluded on the basis of magnetic data is inner orbital octahedral geometry around the metal ion due to donor atom in all the $Ru^{3+}$ complexes.[10, 11]

The electronic spectra of the $Ru^{3+}$ complexes are very interesting in the sense that they can be interpreted in terms of an idealized $D_{4h}$ symmetry of octahedral geometry. The ground state of $Ru^{3+}$ is $^2T_{2g}$ and the first excited doublet level will be $^2A_{2g}(t_{2g})^4(e_g)$ and $^2T_{1g}(t_{2g})^4(e_g)$. In octahedral symmetry the spectra of ruthenium(III) should show the spin allowed d–d bands in the visible region corresponding to the transition $^2T_{1g} \rightarrow {}^2A_{2g}$, $^2T_{2g}$ and $^2T_{1g} \rightarrow {}^2E_g$. Tanabe and Sugano[12] matrices predict eight transitions from the ground state $(t_{2g})^5$ to the doublet states of the configuration $(t_{2g})^4(e_g)^1$ and two transitions from the ground state to the quartet states of $(t_{2g})^4(e_g)^1$. Five bands have been observed in the electronic spectra of each of the present ruthenium(III) complexes in the region 14000–15000 cm$^{-1}$, 18800–19200 cm$^{-1}$, 20500–22000 cm$^{-1}$, 30000–35000 cm$^{-1}$ and 33000–37000 cm$^{-1}$. The second band in the region 18800–19200 cm$^{-1}$ is assigned to $^2T_{2g} \rightarrow {}^2A_{2g}$ transition. If the first band and third band are assigned to the two spin forbidden transitions, then the separation energy between them would correspond to 8B, from which we have to calculate the value of B. Further, the value of 10 Dq is calculated from the ratio Dq/B = 5.1.

TABLE-1
ANALYTICAL DATA ON RUTHENIUM(III) COMPLEXES OF SEMICARBAZONES OF 4-AMINOANTIPYRINE

| Complex | Colour and yield (%) | m.p. (°C) | m.w. | Analysis: Found (Calcd) % | | | $\Omega_m$ | $\mu_{eff}$ |
|---|---|---|---|---|---|---|---|---|
| | | | | Ru | N | Cl | | |
| $Ru(BAAPS)Cl_3$<br>$RuC_{19}H_{20}N_6OCl_3$ | Dark<br>yellow (78) | > 240 d | 555.5 | 17.99<br>(18.18) | 15.00<br>(15.12) | 19.01<br>(19.17) | 2.1 | 1.87 |
| $Ru(HBAAPS)Cl_3$<br>$RuC_{19}H_{20}N_6O_2Cl_3$ | Dark<br>yellow (82) | > 235 d | 571.5 | 17.50<br>(17.67) | 14.58<br>(14.70) | 18.49<br>(18.63) | 1.9 | 1.90 |
| $Ru(MBAAPS)Cl_3$<br>$RuC_{20}H_{22}N_6O_2Cl_3$ | Yellow<br>brown (80) | > 237 d | 585.5 | 17.11<br>(17.25) | 14.23<br>(14.35) | 18.02<br>(18.19) | 2.0 | 1.84 |
| $Ru(DABAAPS)Cl_3$<br>$RuC_{21}H_{25}N_7OCl_3$ | Yellow<br>brown (80) | > 240 d | 598.5 | 16.71<br>(16.87) | 16.20<br>(16.37) | 17.63<br>(17.79) | 1.8 | 1.90 |
| $Ru(2'\text{-}NO_2BAAPS)Cl_3$<br>$RuC_{19}H_{19}N_7O_3Cl_3$ | Reddish<br>yellow (82) | > 240 d | 600.5 | 16.69<br>(16.82) | 16.19<br>(16.32) | 17.59<br>(17.73) | 2.2 | 1.83 |
| $Ru(3'\text{-}NO_2BAAPS)Cl_3$<br>$RuC_{19}H_{19}N_7O_3Cl_3$ | Brownish<br>yellow (82) | > 235 d | 600.5 | 16.67<br>(16.82) | 16.19<br>(16.32) | 17.60<br>(17.73) | 1.7 | 1.88 |
| $Ru(4'\text{-}NO_2BAAPS)Cl_3$<br>$RuC_{19}H_{19}N_7O_3Cl_3$ | Brownish<br>yellow (80) | > 240 d | 600.5 | 16.68<br>(16.82) | 16.17<br>(16.32) | 17.57<br>(17.73) | 2.4 | 1.82 |
| $Ru(HMBAAPS)Cl_3$<br>$RuC_{20}H_{22}N_6O_3Cl_3$ | Deep<br>yellow (82) | > 238 d | 601.5 | 16.63<br>(16.79) | 13.82<br>(13.96) | 17.56<br>(17.70) | 2.3 | 1.89 |
| $Ru(HNAAPS)Cl_3$<br>$RuC_{23}H_{22}N_6O_3Cl_3$ | Dark<br>yellow (78) | > 242 d | 621.5 | 16.14<br>(16.25) | 13.37<br>(13.51) | 17.01<br>(17.13) | 2.1 | 1.90 |
| $Ru(CAAPS)Cl_3$<br>$RuC_{21}H_{22}N_6OCl_3$ | Dark<br>yellow (78) | > 240 d | 581.5 | 17.20<br>(17.37) | 14.32<br>(14.44) | 18.14<br>(18.31) | 1.9 | 1.89 |

$\Omega_m$M in ohm$^{-1}$ cm$^2$ mole$^{-1}$ and $\mu_{eff}$ in B.M.

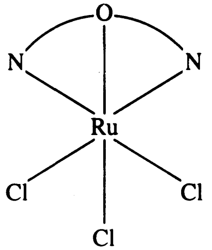
The partial infrared spectral data of the ligands and their Ru$^{3+}$ complexes are given in Table-2. As expected, the $\nu(NH_2)$ band of the hydrazinic nitrogen of semicarbazide (1622 cm$^{-1}$) is absent in the infrared spectra of the semicarbazone[13]. It has also been observed that the amide-II band is shifted towards the lower energy side compared to that of the semicarbazone. The effect is due to the electron density drift from the hydrazinic nitrogen.[14]

TABLE-2
KEY IR BANDS (cm$^{-1}$) OF RUTHENIUM(III) COMPLEXES OF SEMICARBAZONES OF 4-AMINOANTIPYRINE

| Assignments / Compound | ν(C=N) (azomethinic) | ν(C=N) (hydrazinic) | ν(C=O) | | | ν(Ru—N)/ ν(Ru—O) |
|---|---|---|---|---|---|---|
| | | | I | II | III | |
| BAAPS | 1610 m | 1600 m | 1700 s | 1565 s | 1350 s | – |
| Ru(BAAPS)Cl$_3$ | 1585 s | 1625 s | 1652 s | 1530 m | 1332 m | 505 m, 440 w |
| HBAAPS | 1622 m | 1605 m | 1705 s | 1570 s | 1350 m | – |
| RU(HBAAPS)Cl$_3$ | 1596 m | 1630 m | 1642 s | 1535 m | 1332 m | 505 m, 440 m |
| MBAAPS | 1620 m | 1605 s | 1702 s | 1560 m | 1355 m | – |
| Ru(MBAAPS)Cl$_3$ | 1600 m | 1625 s | 1652 s | 1540 m | 1338 m | 510 m, 435 m |
| DABAAPS | 1620 s | 1605 s | 1705 s | 1570 s | 1350 m | – |
| Ru(DABAAPS)Cl$_3$ | 1598 s | 1635 s | 1640 s | 1540 m | 1340 m | 502 m, 450 m |
| 2′-NO$_2$BAAPS | 1612 m | 1602 m | 1700 s | 1565 s | 1340 s | – |
| Ru(2′-NO$_2$BAAPS)Cl$_3$ | 1592 s | 1630 s | 1640 s | 1540 m | 1333 m | 500 m, 435 m |
| 3′-NO$_2$BAAPS | 1608 m | 1600 m | 1702 s | 1565 s | 1340 s | – |
| Ru(3′-NO$_2$BAAPS)Cl$_3$ | 1580 m | 1625 s | 1642 m | 1528 m | 1330 m | 515 m, 442 w |
| 4′-NO$_2$BAAPS | 1610 m | 1600 m | 1705 s | 1562 m | 1355 m | – |
| Ru(4′-NO$_2$BAAPS)Cl$_3$ | 1592 s | 1622 s | 1647 s | 1530 m | 1332 m | 525 m, 437 m |
| HMBAAPS | 1615 m | 1605 m | 1705 s | 1570 s | 1350 m | – |
| Ru(HMBAAPS)Cl$_3$ | 1593 m | 1628 m | 1645 s | 1537 m | 1332 m | 530 m, 432 w |
| HNAAPS | 1608 m | 1600 m | 1702 m | 1565 s | 1342 s | – |
| Ru(HNAAPS)Cl$_3$ | 1582 m | 1627 m | 1650 s | 1532 m | 1322 m | 532 m, 470 w |
| CAAPS | 1610 m | 1600 m | 1700 s | 1572 s | 1350 s | – |
| Ru(CAAPS)Cl$_3$ | 1592 m | 1632 m | 1650 s | 1535 m | 1320 m | 530 m, 472 w |

The characteristic absorption of the carbonyl group in present semicarbazones is observed in 1700–1680 cm$^{-1}$ region[15]. In the complexes, this band is shifted toward lower energy in the 1650–1635 cm$^{-1}$ region. The amide-II band in the free ligands has been observed at *ca.* 1565 cm$^{-1}$. In all the present complexes this band is also shifted towards lower wave numbers by *ca.* 30 cm$^{-1}$. This observation suggests coordination through the carbonyl-oxygen atom. The strong band at *ca.* 1600 cm$^{-1}$ in these semicarbazones apparently has a large contribution from the ν(C=N) mode of semicarbazone moiety[16]. This has been observed as a blue shift in the position of the (C=N) band in all complexes as compared to the free ligands. Another strong band was observed at *ca.* 1610 cm$^{-1}$ due to the azomethine (C=N) absorption. On complexation this band is shifted towards the lower frequency region, clearly indicating the coordination through the azomethime-N atom.[17, 18] In 500–400 cm$^{-1}$ region the bands due to ν(Ru—N)/ν(Ru—O) also appear[10, 11]. ν(Ru—Cl) bands were tentatively assigned to 315–300 cm$^{-1}$ region.[10, 11]

The above discusion clearly indicates that these ligands serve as tridentate ligands, coordinating through the carbonyl-O, hydrozinic-N and azomethinic-N-atoms. On the basis of these studies, the representative structure of the complexes can be shown as follows.



$[Ru(L)Cl_3]$ (C.N. = 6)

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