Asian Journal of Chemistry Vol. 13, No. 2 (2001), 740–744

Some Six-coordinated Rhodium(III) Compounds Derived from Semicarbazones of 4-Aminoantipyrine

LAKSHMAN SINGH*, PRAVIN GUPTA, UPMA SINGH and INDRANIL CHAKRABORTI
Department of Chemistry, Lajpat Rai Postgraduate College, SahiBabad-201 005, India

Semicarbazones usually act as chelating agents with transition metal ions by bonding through the hydrazino-nitrogen and oxygen atoms. Current interest in the coordination chemistry of semicarbazones has arisen through their uses in biological systems. In the present work, we describe the synthesis of rhodium(III) complexes of ten semicarbazones derived from 4-aminoantipyrine and various aryl aldehydes. The complexes were characterized by elemental analyses, magnetic moments, IR and electronic spectral studies. The complexes were found to have the composition [Rh(Ligand)Cl_3]. All the complexes are diamagnetic and are six-coordinated octahedral.

INTRODUCTION

Ruthenium, osmium, rhodium, iridium, palladium and platinum are the heaviest members of group VIII of the periodic table and are rare elements on a terrestrial scale. The chemistry of these elements frequently exhibits common features but wide variations are also frequent. Other than platinum, complexes of rhodium and ruthenium have been the subject of most study, primarily due to their previously established antibacterial activity. The study on rhodium was pioneered by Gillard and coworkers[1, 2], who reported biological activity with complexes of the type *trans* [RhXL]Y, where L = pyridine or other heterocyclic amine ligands, or two bidentate N-donor ligands, such as ethylenediamine, 2,2′-bipyridyl or 1,10-phenanthroline. However, despite many of these complexes causing filamentation of *E. coli,* none of the complexes tested for antitumour activity showed any significant results. In the present work we report the synthesis and characterization of some six-coordinated rhodium(III) compounds derived from semicarbazones of 4-aminoantipyrine, *viz.*, 4[N-(benzalidene) amino] antipyrine semicarbazone (BAAPS), 4[N-(2-hydroxybenzalidene amino] antipyrine · semicarbazone (HBAAPS), 4[N-(4-methoxybenzalidine) amino] antipyrine semicarbazone (MBAAPS), 4[N-(4-dimethyl aminobenzalidine) amino] antipyrine semicarbazone (DABAAPS), 4[N-(2′-nitrobenzalidene) amino] antipyrine semicarbazone (2′-NO_2BAAPS), 4[N-(3′-nitrobenzalidene) amino] antipyrine semicarbazone (3′-NO_2BAAPS), 4[N-(4′-nitrobenzalidene) amino] antipyrine semicarbazone (4′-NO_2BAAPS), 4[N-(4-hydroxy-3-methoxybenzalidene) amino] antipyrine semicarbazone (HMBAAPS), 4[N-(2-hydroxy-1-

zone (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 in two steps:

Step I: A solution of corresponding aromatic aldehyde (1 mmol) in absolute ethanol (20 mL) was mixed with 4-aminoantipyrine (1.1 mmol) in the same solvent (20 mL) and the reaction mixture was refluxed for 2–3 h. On cooling, a yellow crystalline product was separated, which was filtered and recrystallized in the same solvent.

Step II: Semicarbazones were prepared by the method described in the literature. 15 g of semicarbazide hydrochloride and 18 g of sodium acetate were dissolved in 100 mL distilled water and mixed with corresponding Schiff base in equimolar ratio in ethanol. The mixture was refluxed on water bath for 1 h. On cooling the contents, semicarbazone crystallized out. It was filtered and washed with 50% ethanol. The product was recrystallized from ethanol. The light yellow crystals were filtered and dried at *ca.* 60°C in an electric oven.

Preparation of the Complexes: A general method has been used for the preparation of the complexes. A hot aqueous solution (10 mL) of 1 mmol of rhodium(III) chloride was mixed with a hot ethanolic solution (10 mL) of the respective semicarbazone. The reaction mixture was refluxed on a water bath for *ca.* 3 h. On cooling in ice, the desired complex precipitated out. The complex was filtered, washed with 1 : 1 aqueous ethanol and dried over P_4O_{10}.

Physical measurements

Magnetic moments were measured by Gouy balance using $Hg[Co(SCN)_4]$ as calibrating agent. The conductivity measurements were carried out using Toshniwal conductivity bridge, type CL 01/01 and a dip type cell operated at 220 volts AC mains. All the measurements were made at room temperature in nitrobenzene. IR spectra were recorded on Perkin-Elmer-621 automatic recording spectrophotometer. Electronic spectra were recorded in Nujol mull on Perkin-Elmer-524 and Beckmann DK-2 automatic recording spectrophotometer.

Metal content of the complexes was determined by standard method using EDTA as titrant employing Eriochrome Black-T and xylenel orange as indicator, after decomposing the complexes with moderate concentrated sulphuric acid and hydrogen peroxide and dissolving the residue in water and by making necessary volume[4]. The halogens were estimated by Volhard's method[5]. The N-content was analyzed by kjeldahl's method.

RESULTS AND DISCUSSION

The formation of the complexes may be represented by the following reaction:

$$RhCl_3 + L \rightarrow RhLCl_3$$

(L = various semicarbazones used in this study).

Elemental analyses (Table-1) reveal that the complexes have the composition $Rh(L)Cl_3$. The electrical conductivity measurements in $PhNO_2$ (Table-1) show that all the complexes are non-electrolytes and may exist as $[Rh(L)Cl_3]$. All the complexes are diamagnetic as expected. This is inconsistent with an octahedral arrangement of the donor atoms around the metal ion producing a strong field[6, 7].

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

Complex (m.f.)	m.w.	Colour and yield (%)	m.p. (°C)	Analysis, Found (Calcd) %			Λ_m (ohm^{-1} cm^2 $mole^{-1}$)
				Rh	N	Cl	
$Rh(BAAPS)Cl_3$ $(RhC_{19}H_{20}N_6OCl_3)$	557.5	Dark yellow (75)	> 220 d	18.37 (18.47)	14.97 (15.06)	18.93 (19.10)	2.3
$Rh(HBAAPS)Cl_3$ $(RhC_{19}H_{20}N_6O_2Cl_3)$	573.5	Dark yellow (78)	> 230 d	17.82 (17.96)	14.53 (14.65)	18.45 (18.57)	2.1
$Rh(MBAAPS)Cl_3$ $(RhC_{20}H_{22}N_6O_2Cl_3)$	587.5	Brown yellow (80)	> 225 d	17.41 (17.53)	14.19 (14.30)	18.02 (18.13)	2.4
$Rh(DABAAPS)Cl_3$ $(RhC_{21}H_{25}N_7OCl_3)$	600.5	Reddish brown (80)	> 240 d	17.03 (17.15)	16.13 (16.32)	17.60 (17.74)	2.5
$Rh(2'\text{-}NO_2BAAPS)Cl_3$ $(RhC_{19}H_{19}N_7O_3Cl_3)$	602.5	Deep yellow (76)	> 230 d	16.97 (17.09)	16.17 (16.26)	17.52 (17.68)	2.3
$Rh(3'\text{-}NO_2BAAPS)Cl_3$ $(RhC_{19}H_{19}N_7O_3Cl_3)$	602.5	Deep yellow (75)	> 235 d	16.96 (17.09)	16,18 (16.26)	17.53 (17.68)	2.4
$Rh(4'\text{-}NO_2BAAPS)Cl_3$ $(RhC_{19}H_{19}N_7O_3Cl_3)$	602.5	Dark yellow (76)	> 233 d	16.96 (17.09)	16.17 (16.26)	17.55 (17.68)	2.5
$Rh(HMBAAPS)Cl_3$ $(RhC_{20}H_{22}N_6O_3Cl_3)$	603.5	Red brown (80)	> 245 d	16.92 (17.07)	13.80 (13.92)	17.53 (17.65)	2.6
$Rh(HNAAPS)Cl_3$ $(RhC_{23}H_{22}N_6O_3Cl_3)$	623.5	Brown yellow (78)	> 237 d	16.41 (16.52)	13.36 (13.47)	16.93 (17.08)	1.9
$Rh(CAAPS)Cl_3$ $(RhC_{21}H_{22}N_6OCl_3)$	583.5	Dark yellow (75)	> 240 d	17.52 (17.65)	14.28 (14.39)	18.19 (18.25)	2.1

The electronic spectra of the present rhodium(III) complexes show a band in *ca.* 22000 cm^{-1} region and a second band in 31000–32000 cm^{-1} region. These two peaks are due to the expected two spin allowed transitions on account of $(t_{2g})(e_g)$ configuration. The band in 13500–14000 cm^{-1} region is due to the $^1A_{1g} \rightarrow {}^3T_{1g}$ transition and the bands beyond 40000 cm^{-1} are charge transfer ones. The spectra recorded here are very similar to those reported for six-coordinated complexes[8, 9].

The partial infrared spectral data of the ligands and their Rh^{3+} complexes are presented 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[10]. 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[11].

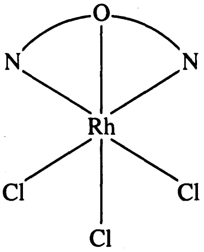
TABLE-2

KEY IR HANDS (cm^{-1}) OF RHODIUM(III) COMPLEXES OF SEMICARBAZONES OF 4-AMINOANTIPYRINE

Assignments / Compound	ν(C═N) (azomethinic)	ν(C═N) (hydrazinic)	ν(C═O)			ν(Rh—N)/ ν(Rh—O)
			I	II	III	
BAAPS	1610 m	1600 m	1700 s	1565 s	1350 s	–
Rh(BAAPS)Cl$_3$	1592 s	1620 s	1645 s	1535 m	1335 s	515 m, 472 w
HBAAPS	1622 m	1605 m	1705 s	1570 s	1350 m	–
Rh(HBAAPS)Cl$_3$	1598 m	1632 m	1645 s	1535 m	1332 m	520 m, 470 m
MBAAPS	1620 m	1605 s	1702 s	1560 m	1355 m	–
Rh(MBAAPS)Cl$_3$	1595 m	1632 s	1648 s	1537 m	1345 m	525 m, 470 m
DABAAPS	1620 m	1605 s	1705 s	1570 s	1350 m	–
Rh(DABAAPS)Cl$_3$	1600 s	1630 s	1645 s	1535 m	1342 m	530 m, 475 m
2′-NO$_2$BAAPS	1612 m	1602 m	1700 s	1565 s	1340 s	–
Rh(2′-NO$_2$BAAPS)Cl$_3$	1595 s	1625 s	1642 s	1532 m	1335 s	532 m, 465 m
3′-NO$_2$BAAPS	1608 m	1600 m	1702 s	1565 s	1340 s	–
Rh(3′-NO$_2$BAAPS)Cl$_3$	1582 m	1630 m	1650 s	1530 m	1325 m	532 m, 472 m
4′-NO$_2$BAAPS	1610 m	1600 m	1705 s	1562 m	1355 m	–
Rh(4′-NO$_2$BAAPS)Cl$_3$	1590 s	1622 s	1645 s	1532 m	1333 m	515 m, 462 w
HMBAAPS	1615 m	1605 m	1705 s	1570 s	1350 m	–
Rh(HMBAAPS)Cl$_3$	1595 m	1630 m	1645 s	1535 m	1332 m	522 m, 460 w
HNAAPS	1608 m	1600 m	1702 m	1565 s	1342 s	–
Rh(HNAAPS)Cl$_3$	1580 m	1628 m	1650 s	1532 m	1322 m	525 m, 462 w
CAAPS	1610 m	1600m	1700 s	1572 s	1350 m	–
Rh(CAAPS)Cl$_3$	1592 m	1630 m	1652 s	1535 m	1320 m	530 m, 460 w

The characteristic absorption of the carbonyl group in present semicarbazones is observed in 1700–1680 cm^{-1} region[12]. In the complexes, this band is shifted toward lower energy in the 1650–1640 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[13]. 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 azomethine-N atom[14, 15]. In 500–400 cm^{-1} region the bands due to ν(Rh—N)/ν(Rh—O) are also observed[7, 16]. ν(Rh—Cl) bands were tentatively assigned at 310–305 cm^{-1} region.

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



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

REFERENCES

1. R. Bromfield, R. Dainty, R. Gillard and B. Heaton, *Nature*, **223**, 735 (1969).
2. R. Gillard, in: T. Conners & J. Roberts (Eds.), Recent Results in Cancer Research, **48**, 29 (1974).
3. B. Beecroft, M.J.M. Campbell and R. Grzeskowiak, *Inorg. Nucl. Chem. Lett.*, **8**, 1097 (1972).
4. F.J. Welcher, The Analytical Uses of Ethylenediamine Tetraacetic Acid, D. Van Nostrand Co., Inc., N.Y. (1965).
5. A.I. Vogel, A Text Book of Quantitative Analysis, Green, London (1961).
6. B.N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, **6**, 37 (1964).
7. Usha and S. Chandra, *Synth. React. Inorg. Met-Org. Chem.*, **22**, 929, 1565 (1992).
8. C.K. Jorgensen, Absorption Spectra and Chemical Bonding in Complexes, Pergamon Press, N.Y. (1964).
9. ————, *Prog. Inorg. Chem.*, **4**, 73 (1962).
10. G. Reed and M. Cohn, *J. Biol. Chem.*, **255**, 662 (1970).
11. H. Levanon, *J. Chem. Phys.*, **49**, 2031 (1968).
12. N.J. Campbell and R. Grzeskowiak, *J. Inorg. Nucl. Chem.*, **30**, 1865 (1968).
13. J.R. Dyer, Application of Absorption Spectroscopy of Organic Compounds, Prentice-Hall, New-Delhi (1984).
14. R.K. Agarwal and R.K. Sarin, *Synth. React. Inorg. Met-Org. Chem.*, **24**, 185 (1994).
15. ————, Polyhedron, **12**, 2411 (1993).
16. Sulekh Chandra, *Synth. React. Inorg. Met-Org. Chem.*, **13**, 89 (1983).

(*Received*: 27 December 2000; *Accepted*: 17 February 2001) AJC-2251