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Synthesis and Characterization of Some Four-Coordinated Pt(II) Coordination Compounds of Semicarbazones Derived from 4-Aminoantipyrine

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In the present work, we describe a novel series of eleven platinum(II) coordination compounds of semicarbazones derived from 4-aminoantipyrine and various aryl aldehydes with the general composition $Pt(L)Cl_2$. All these coordination compounds have been characterized through various physico-chemical studies. The infrared and electronic spectral studies suggest that the ligands act as tridentate (N, N, O) donors and the diamagnetic coordination compounds have square-planar geometries.

INTRODUCTION

Interest in the interaction of platinum metals with biologically important molecules began about 30 years before, when Rosenberg *et al.*[1] published their discovery that certain platnium complexes exhibit anticancer activity. Cisplatin is the parent compound in this group. It is widely used for the treatment of testicular and ovarian cancers, and to a lesser extent, head and neck tumours. The prognosis of this treatment against testicular cancer is usually very good, with five-year disease free survivals for disseminated disease approaching 90%;[2, 3] however, the efficacy of the drug is hampered by severe side-effects, mainly nephrotoxicity, severe nausea and vomiting. The number of platinum complexes which show antitumour activity is still rapidly growing, because of attempts to find complexes with grater potency and reduced toxicity than the existing clinical drugs. In the interest of platinum(II) coordination compounds, in the present work we describe the synthesis and characterization of some four-coordinated platinum(II) coordination 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-methoxy benzalidene) amino] antipyrine semicarbazone (MBAAPS), 4[N-(4-dimethylamino benzalidene) 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 (HMBAAPS), 4[N-(2-hydroxy-1-naphthalidene) amino] antipyrine semicarbazone (HNAAPS), 4[N-(cinnamalidene) amino] antipyrine semicarbazone (CAAPS) and 4[N-(3,4,5-trimethoxy ben-

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zalidene) amino] antipyrine semicarbazone (TMBAAPS). We have already reported the ruthenium(III) and ıhodium(III) coordination compounds with these ligands.[4, 5]

EXPERIMENTAL

Chloroplatinic acid was obtained from Loba Chemicals and was used as supplied. All the eleven semicarbazones of 4-aminoantipyrine were synthesized in the laboratory by reported method.[6, 7]

All the complexes were synthesized according to the following general method. A hot solution (10 mL) of the $H_2[PtCl_4]$ (0.001 mol) was added to a hot ethanolic solution (10 mL) of the respective semicarbazone (0.001 mol). The reaction mixture was refluxed on a water bath for *ca.* 2–3 h.On cooling, a yellow coloured precipitate was obtained in each case. The desired compound was filtered, washed with aqueous ethanol and dried *in vacuo* over P_4O_{10}.

All the physical measurements and analyses were performed as reported eariler[8, 9].

RESULTS AND DISCUSSION

The reaction of Pt^{2+} salt in neutral medium with BAPPS, HBAPPS, MBAAPS, DABAAPS, 2′-NO_2BAAPS, 3′-NO_2BAAPS, 4′-NO_2BAAPS, HMBAAPS, HNAAPS, CAAPS or TMBAAPS gave complexes of the general composition $PT(L)Cl_2$; where L = semicarbazone. All the complexes gave satisfactory elemental results (Table-1). The complexes are quite stable and could be stored for months without any appreciable change. The molar conductance values of $Pt(L)Cl_2$ suggest the 1 : 1 electrolytic nature of these complexes and thus one chloro ion is present outside the coordination sphere. The molecular weight determined cryoscopically in freezing nitrobenzene are in good agreement with the conductance data. All the complexes are diamagnetic in nature and intensely coloured implying a square-planar coordination of the central metal ion by surround ligands. It is well known[8, 9] that metal ions such as Pt^{2+} having a d^8 configuration favour the formation of complexes with square-planar geometry. The electronic spectra of Pt^{2+} complexes positively affirm the presence of square-planar geometry in these complexes. Three d-d spins allowed transitions are expected corresponding to the transitions from the three lower lying d-levels to the empty $d_{x^2-y^2}$ orbitals. The ground state is $^1A_{2g}$ and the excited states corresponding to these transitions are $^1A_{2g}$, $^1B_{1g}$ and ^1E_g in increasing order of energy. The electronic spectral bands appearing in 25000–22000 cm^{-1} region in present complexes may be assigned to the $^1A_{1g} \rightarrow {}^1B_{1g}$ transition. Other electronic spectral bands appearing at *ca.* 28000 cm^{-1} and above are due to charge transfer.

The key infrared spectral bands of the ligands and their Pt^{2+} 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 semicar-

TABLE-1

ANALYTICAL DATA ON PLATINUM(II) COMPLEXES OF SEMICARBAZONES OF 4-AMINOANTIPYRINE

Compounds (Empirical formula)	Color and yield (%)	m.p. (°C)	m.w.	% Analysis: Found (Calcd.)			Λ_m (ohm^{-1} cm^2 mole^{-1})
				Pt	N	Cl	
Pt(BAAPS)Cl_2 ($PtC_{19}H_{20}N_6OCl_2$)	Dark brown (70)	> 235 d	614	31.53 (31.75)	13.44 (13.68)	11.40 (11.56)	25.6
Pt(HBAAPS)Cl_2 ($PtC_{19}H_{20}N_6O_2Cl_2$)	Reddish brown (65)	> 230 d	630	30.79 (30.95)	13.09 (13.33)	11.07 (11.26)	29.2
Pt(MBAAPS)Cl_2 ($PtC_{20}H_{22}N_6O_2Cl_2$)	Reddish brown (57)	> 235 d	644	30.19 (30.27)	12.96 (13.04)	10.95 (11.02)	30.1
Pt(DABAAPS)Cl_2 ($PtC_{21}H_{25}N_7OCl_2$)	Blackish brown (75)	> 230 d	657	29.49 (29.68)	14.79 (14.91)	10.67 (10.80)	28.7
Pt(2′-NO_2BAAPS)Cl_2 ($PtC_{19}H_{19}N_7O_3Cl_2$)	Reddish brown (60)	> 228 d	659	29.39 (29.59)	14.68 (14.87)	10.59 (10.77)	24.3
Pt(3′-NO_2BAAPS)Cl_2 ($PtC_{19}H_{19}N_7O_3Cl_2$)	Dark brown (65)	> 230 d	659	29.40 (29.59)	14.67 (14.87)	10.58 (10.77)	26.9
Pt(4′-NO_2BAAPS)Cl_2 ($PtC_{19}H_{19}N_7O_3Cl_2$)	Cherry brown (62)	> 235 d	659	29.35 (29.59)	14.69 (14.87)	10.58 (10.77)	27.3
Pt(HMBAAPS)Cl_2 ($PtC_{20}H_{22}N_6O_3Cl_2$)	Dark brown (67)	> 240 d	660	29.30 (29.54)	12.59 (12.72)	10.53 (10.75)	27.9
Pt(HNAAPS)Cl_2 ($PtC_{23}H_{22}N_6O_3Cl_2$)	Brown (65)	> 237 d	696	27.83 (28.01)	11.87 (12.06)	10.04 (10.20)	25.8
Pt(CAAPS)Cl_2 ($PtC_{21}H_{22}N_6OCl_2$)	Brown (68)	> 230 d	640	30.29 (30.46)	13.02 (13.12)	10.86 (11.09)	26.8
Pt(TMBAAPS)Cl_2 ($PtC_{22}H_{26}N_6O_4Cl_2$)	Brown (65)	> 240 d	704	27.49 (27.69)	11.79 (11.93)	9.94 (10.08)	24.9

bazone[15]. 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.[16]

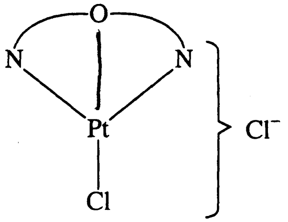
TABLE-2

KEY IR BAND (cm^{-1}) OF PLATINUM(II) COMPLEXES OF SEMICARBAZONES OF 4-AMINOANTIPYRINE

Assignements / Compounds	ν(C=N) (azo-methinic)	ν(C=N) (hydra-zinic)	ν(C=O)			ν(Pt-N)/ ν(Pt-O)
			I	II	III	
BAAPS	1610 m	1600 m	1700 s	1565 s	1350 s	–
Pt(BAAPS)Cl$_2$	1582 s	1630 m	1650 s	1532 m	1332 m	535 m, 445 w
HBAAPS	1622 m	1605 m	1705 s	1570 s	1350 m	–
Pt(HBAAPS)Cl$_2$	1595 m	1635 m	1645 s	1537 m	1332 m	532 m, 440 w
MBAAPS	1620 m	1605 m	1702 s	1560 m	1355 m	–
Pt(MBAAPS)Cl$_2$	1598 m	1630 s	1650 s	1542 m	1340 m	540 m, 437 w
DABAAPS	1620 s	1605 s	1705 s	1570 s	1350 m	–
Pt(DABAAPS)Cl$_2$	1595 s	1635 s	1640 s	1540 m	1337 m	537 m, 435 w
2′-NO$_2$BAAPS	1612 m	1602 m	1700 s	1565 s	1340 m	–
Pt(2′-NO$_2$BAAPS)Cl$_2$	1593 s	1632 s	1645 s	1540 m	1330 m	535 m, 445 w
3′-NO$_2$BAAPS	1608 m	1600 m	1702 s	1565 s	1340 s	–
Pt(3′-NO$_2$BAAPS)Cl$_2$	1582 m	1630 s	1645 s	1528 m	1332 m	545 m, 450 w
4′-NO$_2$BAAPS	1610 m	1600 m	1705 s	1562 m	1355 m	–
Pt(4′-NO$_2$BAAPS)Cl$_2$	1590 s	1622 s	1648 s	1530 m	1332 m	530 m, 437 w
HMBAAPS	1615 m	1605 m	1705 s	1570 s	1350 m	–
Pt(HMBAAPS)Cl$_2$	1590 m	1628 m	1645 s	1537 m	1332 m	535 m, 457 w
HNAAPS	1608 m	1600 m	1702 s	1565 s	1342 s	–
Pt(HNAAPS)Cl$_2$	1580 m	1628 m	1650 s	1532 m	1322 m	540 m, 442 w
CAAPS	1610 m	1600 m	1700 s	1572 s	1350 s	–
Pt(CAAPS)Cl$_2$	1592 m	1632 m	1650 s	1535 m	1325 m	542 m, 440 w
TMBAAPS	1615 s	1600 s	1700 s	1565 m	1350 m	–
Pt(TMBAAPS)	1585 s	1622 s	1645 s	1535 m	1335 m	530 m, 430 w

The characteristic absorption of the carbonyl group in present semicarbazones is observed in 1700–1680 cm^{-1} region[17]. In these 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 in 1570–1560 cm^{-1} region. In all the present complexes this band is also shifted towards lower wave numbers of *ca.* 30 cm^{-1}. This observation suggests coordination through the carbonyl-oxygen atom. The strong band in the 1605–1600 cm^{-1} region in these semicarbazones apparently has a large contribution from the ν(C=N) mode of semicarbazone moiety[18]. 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[19, 20]. In 550–430 cm^{-1} region the bands due to ν(Pt—N)/ν(Pt—O) also appear[8, 9].

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:



[Pt(L)Cl]Cl (C.N. = 4)

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