

## METAL COMPLEXES OF 6-ETHOXY-2-AMINO BENZOTHAZOLE

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## ABSTRACT

Complex compounds of the platinum metals with 6-ethoxy-2-aminobenzothiazole (L),  $ML_2X_2$  ( $M = Pd, Pt; X = Cl, Br$ ),  $[RhL_3Cl_3] \cdot 3H_2O$ ,  $[IrL_2Cl_3 \cdot H_2O] \cdot 2H_2O$  and  $[RuL_3Cl_2(OH)]$  have been isolated and characterized by electrical conductivity, magnetic susceptibility and IR spectral measurements. The ruthenium(III) complex is paramagnetic, having the normal magnetic moment value of 1.95 B.M. Infrared evidence indicates that the ligand is bonded to the metal atoms through the ring nitrogen atom.

## INTRODUCTION

**2-S**UBSTITUTED benzothiazoles are shown to be active against dermatophytes, protozoans, gram-positive bacteria and even against the bacterial strains which are resistant to penicillin and viruses<sup>1</sup> and fungicidal activity of 2-amino derivatives of benzothiazoles is well known<sup>2</sup>. Several complexes of 2-substituted benzimidazole, benzoxazole and benzothiazole also have been found to possess antibacterial activity<sup>3</sup>. The recent discovery of anti-neoplastic and anti-viral properties of complexes of the platinum metals has prompted extensive investigation of the oncological potentialities of coordination compounds of these metals with a variety of ligands<sup>4</sup> including thiazoles<sup>5</sup>. The anti-tumour activity of rhodium complex of 6-methoxy-2-aminobenzothiazole has been investigated recently<sup>6</sup>. Therefore, the complexes of 6-ethoxy-2-aminobenzothiazole with the platinum metals may also be expected to exhibit biologically significant characteristics. In addition to the biological potentiality, the ligand, 6-ethoxy-2-aminobenzothiazole, has a theoretically interesting aspect as a potential ambidentate ligand which may bind through the endo- or exo-cyclic nitrogen or the sulphur atom. There is the further possibility of amino-imino tautomerism which may lend a chelating character to the ligand.

A few substituted derivatives of 2-aminobenzothiazole such as 4-chloro- and 4-methyl-2-aminobenzothiazole, 5-ethoxy-2-aminobenzothiazole and 6-chloro- and 6-methyl-2-aminobenzothiazole have been used as ligands<sup>7-11</sup>. As the donor site in 6-chloro- and 6-methyl-2-aminobenzothiazole<sup>9, 10</sup> was found to be different from that of 2-aminobenzothiazole, it was considered interesting to investigate the

coordination behaviour of 6-ethoxy-2-aminobenzothiazole.

## EXPERIMENTAL

*Materials:* 6-Ethoxy-2-aminobenzothiazole of Koch-Light, practical grade, was recrystallized from ethanol and dried over fused  $CaCl_2$ .  $PdCl_2$ ,  $RhCl_3 \cdot 3H_2O$ ,  $IrCl_3 \cdot 3H_2O$  and  $RuCl_3 \cdot 3H_2O$  of Johnson Matthey, England, and  $K_2PtCl_4$  of Arora Matthey, Calcutta, were used as such. Palladium bromide was prepared by dissolving freshly precipitated palladium hydroxide in 48% HBr. The solution was slowly evaporated on a water bath and finally dried over fused  $CaCl_2$ .

*Preparation of the complexes:*

*Dichloro-bis(6-ethoxy-2-aminobenzothiazole) palladium(II).* An aqueous solution of  $PdCl_2$  (1 mmol, 0.213 g) was added to an ethanolic solution of 6-ethoxy-2-aminobenzothiazole (4 mmol, 0.852 g). On warming a yellow solid separated which was filtered, washed successively with water, ethanol and ether and dried under IR lamp. Yield: 98%.

*Dibromo-bis(6-ethoxy-2-aminobenzothiazole) palladium(II).* An aqueous solution of palladium bromide (1 mmol, 0.302 g) containing a little hydrobromic acid was added to the ethanolic solution of 6-ethoxy-2-aminobenzothiazole (4 mmol, 0.852 g). The remaining procedure was the same as for the corresponding chloro complex. Yield: 40%.

*Dichloro-bis(6-ethoxy-2-aminobenzothiazole) platinum(II).* The grey complex was prepared from  $K_2PtCl_4$  and the ligand by a procedure similar to that

for the corresponding complex of palladium. Yield: 63%.

*Dibromo-bis(6-ethoxy-2-aminobenzothiazole) platinum(II)*. An excess of KBr (~ 0.75 g) was added to an aqueous solution of potassium chloroplatinate(II) (1 mmol, 0.415 g). The mixture was gently warmed and added to an ethanolic solution of the ligand (4 mmol, 0.852 g). A greyish green solid formed, which was filtered and washed successively with water, ethanol and ether. Yield: 64%.

*Trichloro-tris(6-ethoxy-2-aminobenzothiazole) rhodium(III) trihydrate, aquotrichloro-bis(6-ethoxy-2-aminobenzothiazole) iridium(III) dihydrate and dichlorohydroxo-tris(6-ethoxy-2-aminobenzothiazole) ruthenium(III)*. The complexes were similarly isolated from the metal chlorides and the ligand in 1:3 molar ratio.

#### Analysis of the complexes:

C, H and N were microanalyzed at CDRI, Lucknow. Sulphur and halogens were determined by fusion and precipitation as BaSO<sub>4</sub> and silver halides respectively. Palladium was estimated as palladium dimethylglyoximate. Platinum was determined as metal by ignition. Rhodium, iridium and ruthenium were weighed as metals on ignition and subsequent reduction in hydrogen<sup>12</sup>.

#### Physical measurements:

Infrared spectra were measured on Perkin Elmer 577 spectrophotometer in the region 200–4000 cm<sup>-1</sup>

as caesium iodide discs. Electrical conductivity was measured with a Phillips Conductivity Meter, model PR 9500/90. Magnetic measurements were performed on a Gouy balance.

## RESULTS AND DISCUSSION

The compounds isolated, the data on their elemental analyses and their main infrared bands are listed in tables 1 and 2 respectively. The electrical conductivity values in DMF or acetone reveal their non-electrolytic nature in solution. The ruthenium complex has a magnetic moment of 1.95 B.M., which shows the presence of one unpaired electron indicating the trivalent state of the metal.

#### Infrared Spectra

(a) *Palladium and platinum complexes*: On comparing the spectra of 2-aminobenzothiazole and 6-ethoxy-2-aminobenzothiazole, a strong, split band near 1630 cm<sup>-1</sup> is assigned as  $\delta_{\text{NH}_2}$ . This suffers a large negative shift on complexation. The antisymmetric and the symmetric  $\nu_{\text{NH}_2}$  bands of the ligand (around 3400 and 3200 cm<sup>-1</sup>) are affected only slightly in the complexes. It is generally observed that coordination through amino group involves a positive shift in  $\delta_{\text{NH}_2}$  and a negative shift in  $\nu_{\text{NH}_2}$  bands<sup>13</sup>. Therefore, bonding through the amino group is less likely in these complexes. The strong  $\nu_{\text{C=N}}$  band at 1535 cm<sup>-1</sup> in the ligand<sup>14</sup> remains almost unshifted in PdL<sub>2</sub>Cl<sub>2</sub> and moves only slightly to lower frequencies in PdL<sub>2</sub>Br<sub>2</sub> as well as in the chloro and bromo complexes of platinum. The C–S stretching frequency of the ligand<sup>15</sup> at 610 cm<sup>-1</sup> is shifted to higher frequencies in the

Table 1 Analytical data and molar conductivities ( $A_M$ ) of complexes of 6-ethoxy-2-aminobenzothiazole

Complex	Conductivity ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>	% Found (calculated)					
		M	C	H	N	S	X
PdL <sub>2</sub> Cl <sub>2</sub>	50.3	18.4 (18.7)	39.3 (38.2)	3.5 (3.5)	9.5 (9.9)	11.6 (11.3)	12.2 (12.5)
PdL <sub>2</sub> Br <sub>2</sub>	61.1	16.0 (16.3)	33.7 (33.0)	3.0 (3.0)	8.2 (8.5)	9.7 (9.7)	24.0 (24.4)
PtL <sub>2</sub> Cl <sub>2</sub>	18.9	29.6 (29.8)	33.9 (33.0)	3.1 (3.0)	8.3 (8.5)	8.8 (9.7)	10.2 (10.8)
PtL <sub>2</sub> Br <sub>2</sub>	26.0	26.0 (26.2)	30.0 (29.0)	3.0 (2.6)	7.0 (7.5)	8.8 (8.6)	21.7 (21.5)
[RhL <sub>3</sub> Cl <sub>3</sub> ]·3H <sub>2</sub> O	25.5	11.5 (12.1)	39.3 (38.3)	3.5 (4.2)	9.6 (9.9)	11.0 (11.3)	11.7 (12.5)
[IrL <sub>2</sub> Cl <sub>3</sub> ·H <sub>2</sub> O]·2H <sub>2</sub> O	31.1	25.2 (25.9)	30.0 (29.1)	3.1 (3.5)	7.8 (7.5)	9.3 (8.6)	14.7 (14.3)
[RuL <sub>3</sub> Cl <sub>2</sub> (OH)]	16.4	12.4 (13.0)	42.5 (42.0)	3.0 (2.7)	10.5 (10.8)	12.2 (12.4)	10.1 (9.2)

Table 2 Principal IR bands ( $\text{cm}^{-1}$ ) of 6-ethoxy-2-aminobenzothiazole(L) and its complexes

L	3415 vs 3400	3275 s, br	1632 vs 1626	1535 s, br 1515 sh	1340 s, br	610 ms, br	—
$\text{PdL}_2\text{Cl}_2$	3396 s 3356	3280 s, br	1595 vs, br	1535 s, br	1347 s 1327	623— 610 m, br	385 m, mbr 278 mw, br 280 w, sp
$\text{PdL}_2\text{Br}_2$	3410 ms, br	3285 s, br	1594 vs, br	1529 ms, sp	1335 sh 1329 m, br	625 mw, br	—
$\text{PtL}_2\text{Cl}_2$	3380 s, br	3278 s, br	1597 s, mbr	1525 ms, br	1345 m, br	638 mw, br	238 mw, sp 224 mw, sp
$\text{PtL}_2\text{Br}_2$	3408— 3320 m, br	3275 m, br	1597 s, br	1525 m, br	1347— 1332 m, br	638 w, br	230 m, sp
$[\text{RhL}_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$	3440— 3385 m, br	3290— 3260 s, br	1605 s, br	1520 ms, br	1343 m, br	653— 638 w, br	260 mw, sp 250 ms, sp 225 ms, sp
$[\text{IrL}_2\text{Cl}_3 \cdot \text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$	3540— 3380 s, br	3272— 3260 s, br	1605 s, br	1528— 1505 w, br	1340 mw, br	640 w, br	230 mw, sp 210 mw, sp
$[\text{RuL}_3\text{Cl}_2(\text{OH})]$	3640— 3380 m, br	3260— 3230 s, br	1578 vs, br	1484 sh	1356 m, br	640 w, br	248 m, sp 230 m, sp 210 m, sp
Band assignment	$\nu_{\text{OH}} + \nu_{\text{NH}_2(\text{asym})}$	$\nu_{\text{NH}_2(\text{sym})}$	$\delta_{\text{NH}_2}$	$\nu_{\text{C}=\text{N}}$	$\nu_{\text{C}=\text{NH}_2}$	$\nu_{\text{C}=\text{S}}$	$\nu_{\text{M}=\text{X}}$ $\nu_{\text{M}=\text{N}}$

complexes. It is generally observed that coordination through ring nitrogen brings about a decrease in  $\nu_{C=N}$  and an increase in  $\nu_{C-S}$  of benzothiazoles<sup>16, 17</sup>. As a slight negative shift is seen in  $\nu_{C=N}$  and a positive shift in  $\nu_{C-S}$  bands of the ligand in these complexes, it is felt that the ligand is bonded through the ring nitrogen atom.

The palladium chloro complex shows two bands for  $\nu_{Pd-Cl}$  at 385 and 368  $cm^{-1}$  and for  $\nu_{Pd-N}$  at 288 and 278  $cm^{-1}$ , indicating a cis-configuration for the complex. Normally the square planar complexes of palladium tend to assume a trans-configuration but examples of cis-configuration are also known<sup>18</sup>. In the palladium bromo complex, weak bands at 280  $cm^{-1}$  and 265  $cm^{-1}$  are assigned as  $\nu_{Pd-N}$  and  $\nu_{Pd-Br}$  respectively. The bromo complex is thus probably in a trans-configuration.  $PtL_2Cl_2$  has a medium intensity and broad band at 370  $cm^{-1}$  with a shoulder at 338  $cm^{-1}$  and two medium intensity bands at 238 and 224  $cm^{-1}$ , which are attributed as  $\nu_{Pt-Cl}$  and  $\nu_{Pt-N}$  respectively. The corresponding bromo complex shows a weak band at 260  $cm^{-1}$  and a medium intensity band at 230  $cm^{-1}$  which may be assigned as Pt-Br and Pt-N stretching modes respectively.

(b) *Rhodium, iridium and ruthenium complexes*: The IR spectra of these complexes exhibit a very broad band in the 3640–3380  $cm^{-1}$  region indicating the presence of water or coordinated hydroxyl groups in the complexes. The asymmetric  $\nu_{NH_2}$  band expected around 3400  $cm^{-1}$  is enveloped by the broad  $\nu_{OH}$  band. The symmetric  $\nu_{NH_2}$  band of the ligand at 3278  $cm^{-1}$  suffers very little shift in the complexes which is an indication of the non-coordinated amino group; the broadening of symmetric  $\nu_{NH_2}$  band in the complex is possibly due to hydrogen bonding effects. As discussed above, the N–H deformation mode of the ligand shows a decrease (27 to 54  $cm^{-1}$ ) in frequency in the complexes. Therefore, it is less likely that bonding occurs through the amino group. The intensity of C–N stretching mode of the ligand is weakened as well as shifted to lower frequencies in these complexes which indicates the linkage through the ring nitrogen atom; the increase in C–S stretching mode also supports the coordination through ring nitrogen. The complexes exhibit multiple bands in 250–200  $cm^{-1}$  region and the ligand also shows two bands in the same region, however, the bands which are additionally present at 260, 250 and 225  $cm^{-1}$  in the rhodium complex, at 230 and 210  $cm^{-1}$  in the iridium complex and at 248, 230 and 210  $cm^{-1}$  in the ruthenium complex, may be assigned as  $\nu_{M-N}$ . The presence of three  $\nu_{M-N}$  bands

indicate the trans-configuration of the rhodium complex<sup>19</sup>. In the rhodium chloro complex the bands at 345, 330 and 312  $cm^{-1}$  are attributed to  $\nu_{Rh-Cl}$ . Iridium complex exhibits  $\nu_{Ir-Cl}$  at 305  $cm^{-1}$  and ruthenium complex shows a broad band at 305  $cm^{-1}$  with shoulder at 328  $cm^{-1}$  assigned as  $\nu_{Ru-Cl}$ .

Complexes of 2-aminobenzothiazole with Co(II), Cu(II), Cd(II) and Hg(II) have been shown to contain M–N (ring) linkage<sup>8</sup>. 4-Chloro- and 4-methyl-2-aminobenzothiazoles have also been shown to coordinate through the ring nitrogen in their complexes to Co, Cu, Cd and Hg<sup>8</sup>. As the chloro- and methyl groups have opposite electronic effects, it appears that the mode of linkage of 2-aminobenzothiazole is not affected seriously by the electronic effects of the substituents at 4-position.

In the case of 6-substituted 2-aminobenzothiazoles a different mode of linkage has been suggested<sup>9, 10</sup>. Both 6-chloro- and 6-methyl-2-aminobenzothiazoles were found to be linked through the sulphur atom indicating that the opposite inductive effects of chloro and methyl groups are again of no consequence. However, as discussed above, our results strongly suggest that 6-ethoxy-2-aminobenzothiazole coordinates to the platinum metals through ring nitrogen. This appears to be in line with the mode of linkage suggested in the Pd(II) and Pt(II) complexes of 2-aminobenzothiazole<sup>20</sup>.

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## NEWS

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### SOUNDTRACK MIXING: ADVANCED

Advanced sound-mixing consoles, specifically designed for film-soundtrack production, have been developed by a British company. The 60-channel multi-track recording and film scoring console for sound-dubbing 35 mm and 70 mm film incorporates a number of special features.

These include joystick-type pan pots routing to four-track outputs; four-loudspeaker monitoring for left, centre, right and ambience; and additional talk-back facilities to projector rooms.

The console consists of 60-input modules, incorporating the company's Formant Spectrum Equalisation

system (F.S.E), and the newly developed inline dynamics unit. Full 48-track routing is featured and metering is achieved on 48 bargraph-type meters. A total of 120 inputs may be routed to the four-track mix outputs. Large and small faders are provided on each input strip, interchangeable on an individual or master basis using soft switching techniques.

Further details may be had from: Mrinalini Raghavan, Assistant Commercial Information Officer, British High Commission, Chanakyapuri, New Delhi 110021.

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### FIRST ADVANCED, LARGE-DIAMETER SILICON FURNACE IN U.S. OPENS IN PITTSBURGH

Westinghouse Electric Corporation has opened a \$2-million facility at its Research and Development Center at Pittsburgh for research in the production of ultrahigh-purity silicon for electronic devices. This is the largest float-zone crystal growth furnace in the U.S. Float-zone research—in which the silicon is purified by magnetic levitation—is aimed at the production of high-quality single-crystal silicon for both advanced power semiconductor devices and speciality integrated circuits. The Westinghouse furnace can produce single crystals in rods up to five inches in

diameter and four feet long. The float-zone furnace facility is expected to become a leading center for research in the production of ultrahigh-purity silicon. It is "an example of the increased cooperative efforts of industry with government toward the improving the technological health of the United States."

Further details may be had from: Robert J. Benke, Westinghouse Electric Corporation, Westinghouse Building, Gateway Center, Pittsburgh, Pennsylvania 15222.

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