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Synthesis and Characterization of New Platinum(II) Complexes Containing Thiazole and Imidazole Donors
II.* Tribromo(styrylheterazole)platinate(II) Anionic Complexes**

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Abstract

Platinum(II) complexes of the type $[NEt_4][Pt(L)Br_3]$, where L is a styrylbenzoheterazole derived from imidazole, thiazole, oxazole or selenazole, have been prepared. The complexes were characterized by their melting points, elemental analyses, UV–Vis spectra and far-infrared spectra. The crystal and molecular structures of two of the complexes were determined by X-ray diffraction techniques. These complexes have square planar geometry about the Pt atom, with the ligands coordinated to the Pt through the N of the heterocyclic rings.

Introduction

Since the discovery by Rosenberg *et al.* [2, 3] of the antitumor activity of *cis*-diamminedichloroplatinum(II), *cis*-DDP, platinum(II) amine complexes have been widely studied [4, 5]. Variations in the nature of the amine can have a significant effect on the activity and toxicity of these complexes. N-heterocyclic ligands such as imidazole, thiazole and benzoxazole [6–11] have been used for the synthesis of new complexes. Recently the new mixed complexes *cis*-$[Pt(NH_3)(L)Cl_2]$, incorporating thiazole, benzothiazole and imidazole derivatives, some of which showed significant cytotoxicity, were reported [1]. Since Schiff bases derived from thiazoles and benzothiazoles [12] and derivatives of the styrylbenzothiazoles [13] have shown biological activity, it seemed of interest to study different types of Pt(II) complexes of these biologically active ligands to see if new or enhanced modes of activity might be observed. This paper reports the synthesis and characterization of complexes of the type $[NEt_4][Pt(L)Br_3]$, where L is a styrylbenzoheterazole derivative which contains thiazole, imidazole, oxazole or selenazole. In subsequent papers we will describe other types of complexes, cytotoxicity tests and possible structure–activity relationships for the complexes and the ligands.

The ligands used were: 2-(2′-chloro-5′-nitrostyryl)benzothiazole (nsb, **1**, $X = S$, $R_1 = R_2 = R_3 = H$), *cis*-2-(2′-chloro-5′-nitrostyryl)benzothiazole (*cis*-nsb, **1** with *cis* olefinic link, $R_1 = R_2 = R_3 = H$), 2-(2′-chloro-5′-nitrostyryl)benzoxazole (nsbo, **1**, $X = O$, $R_1 = R_2 = R_3 = H$), 2-(2′-chloro-5′-nitrostyryl)benzoselenazole (nsbse, **1**, $X = Se$, $R_1 = R_2 = R_3 = H$), 2-(2′-chloro-5′-nitrostyryl)-α-acetoxybenzothiazole (a-nsb, **1**, $X = S$, $R_1 = R_2 = H$, $R_3 = CH_3CO_2^-$), 2-(2′-chloro-5′-nitrostyryl)-α-cyanobenzothiazole (cn-nsb, **1**, $X = S$, $R_1 = R_2 = H$, $R_3 = CN^-$), 2-(2′-chloro-5′-nitrostyryl)-6,7-dimethoxybenzothiazole (dmensb, **1**, $X = S$, $R_1 = R_2 = CH_3O^-$, $R_3 = H$), 2-(2′-chloro-4′-nitrostyryl)benzothiazole (4-nsb, **2**, $R_1 = H$, $R_2 = Cl$, $R_3 = NO_2$), 2-(2′-chloro-4′-nitrostyryl)-6-methoxybenzothiazole (me-4-nsb, **2**, $R_1 = CH_3O^-$, $R_2 = Cl$, $R_3 = NO_2$), 2-(2′-hydroxystyryl)benzothiazole (ohsb, **2**, $R_1 = H$, $R_2 = OH$, $R_3 = H$), 2-(2′-acetoxystyryl)benzothiazole (asb, **2**, $R_1 = H$, $R_2 = CH_3CO_2^-$, $R_3 = H$), 2-(2′-chlorostyryl)benzothiazole (csb, **2**, $R_1 = H$, $R_2 = Cl$, $R_3 = H$), 2-(2′-chloro-5′-nitrostyryl)benzimidazole (nsbiz, **3**, $R_1 = H$, $R_2 = NO_2$), 2-(2′-chloro-5′-nitrostyryl)-1-methylbenzimidazole (me-nsbiz, **3**, $R_1 = CH_3$, $R_2 = NO_2$), 2-(2′-chloro-5′-nitrostyryl)-1-ethylbenzimidazole (et-nsbiz, **3**, $R_1 = C_2H_5$, $R_2 = NO_2$), 2-(2′-chloro-5′-nitrostyryl)-1-isopropylbenzimidazole (ipr-nsbiz, **3**, $R_1 = \text{iso-}C_3H_7$, $R_2 = NO_2$), 2-(2′-chloro-5′-nitrostyryl)-1-n-butyl-benzimidazole (nbu-nsbiz, **3**, $R_1 = \text{n-}C_4H_9$, $R_2 = NO_2$), 2-(2′-chloro-5′-nitrostyryl)-1-benzylbenzimidazole (bz-nsbiz, **3**, $R_1 = CH_2C_6H_5$, $R_2 = NO_2$) and 2-(2′-chlorostyryl)-1-ethylbenzimidazole (et-csbiz, **3**, $R_1 = C_2H_5$, $R_2 = H$). The styrylbenzoheterazole ligands are potentially ambidentate with either N or S available for coordination, so structure determination is of interest. Structures of two complexes, $[NEt_4]$-

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*For Part I, see ref. 1.

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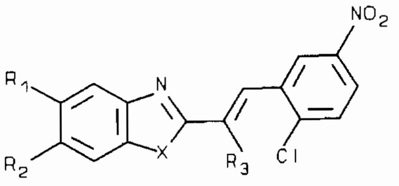

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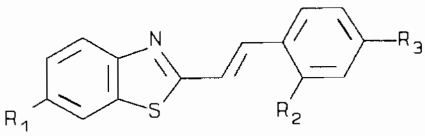

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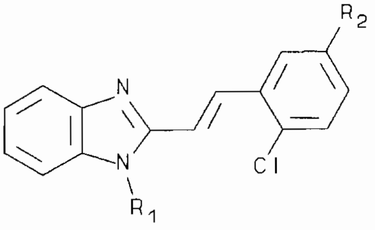

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$[Pt(csb)Br_3]$ and $[NEt_4][Pt(me\text{-}4\text{-}nsb)Br_3]$, are reported here; others ($[NEt_4][Pt(nsb)Br_3]$ [14], $[NEt_4][Pt(asb)Br_3]$ [15] and *cis*-$[Pt(asb)_2Cl_2]$ [16]) have been reported recently.

Experimental

Physical Measurements

Ultraviolet visible spectra were recorded using a Perkin-Elmer Lambda 4B UV–Vis spectrophotometer. Far-IR spectra (500–200 cm^{-1}) as Nujol mulls between polyethylene disks were recorded using a Nicolet 6000 series 80 spectrophotometer. Melting points (uncorrected) were measured in capillary tubes using a Thomas Hoover Capillary Melting Point Apparatus. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

Starting Materials

Syntheses of the styrylbenzoheterazole ligands by Cox *et al.* followed previously reported methods [13] and will be described elsewhere [17]. $[NEt_4]$-$[Pt_2Br_6]$ was prepared from K_2PtCl_4 (Strem Chem. Co.) [18]. All solvents (CH_3CN, CH_3COCH_3), EtOH, MeOH) were distilled and dried.

Syntheses of the Complexes: General Procedure

Tetraethylammonium Tribromo[2-(2′-chloro-5′-nitrostyryl)benzothiazole]platinate(II), [NEt$_4$][Pt(nsb)Br$_3$]

An acetone solution (10 ml) of 0.056 g (0.178 mmol) of 2-(2′-chloro-5′-nitrostyryl)benzothiazole was added slowly to 10 ml of an acetone solution of 0.100 g (0.088 mmol) of $[NEt_4]_2[Pt_2Br_6]$. The reaction mixture was stirred and heated on a hot plate at about 50 °C for 30 min and then left to evaporate at room temperature. The solid obtained was washed several times with ether in order to remove unreacted ligand. A yellow powder was obtained which yielded 92% of $[NEt_4][Pt(nsb)Br_3]$, which was recrystallized from nitromethane.

All the other complexes were prepared according to the same general procedure, using the same stoichiometric ratios and solvents, unless otherwise noted in Table 1.

Collection and Refinement of X-ray Data

Diffraction data were collected using an Enraf-Nonius CAD4 diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å) and an incident beam graphite monochromator. The crystals were mounted on a glass fiber. All data were collected at room temperature. Crystal data and other information for $[NEt_4]$-$[Pt(csb)Br_3]$ and $[NEt_4][Pt(me\text{-}4\text{-}nsb)Br_3]$ are summarized in Table 2. Corrections were made for absorption and Lorentz–polarization effects. Anomalous dispersion terms were also included in the calculations. Structures were solved with the Enraf-Nonius Structure Determination Package [19].

[NEt$_4$][Pt(csb)Br$_3$]

An orange prismatic crystal having approximate dimensions of 0.40 × 0.40 × 0.20 mm was mounted on a glass fiber with its long axis roughly parallel to the phi axis of the goniometer. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $6 < \theta \leqslant 13°$. The complex crystallized in the monoclinic group $P2_1/n$ with $Z = 4$. Cell parameters were $a = 14.371(4)$, $b = 10.043(6)$, $c = 20.294(4)$ Å, $\beta = 110.16(3)°$, $V = 2750(4)$ Å^3, $D_{calc} = 2.02$ g cm^{-3}. Systematic absences $0k0$ ($k = 2n + 1$), $h0l$ ($h + l = 2n + 1$); $+h, +k, \pm l$ with $h \leqslant 18$, $k \leqslant 12$, $|l| \leqslant 25$. A total of 5909 unique reflections were measured, 3288 with $F^2 > 2\sigma(F_0)^2$. Absorption corrections from psi-scans were applied and the relative transmission coefficients were found to range from 0.403 to 0.999. The linear absorption coefficient (μ) for this compound using Mo Kα radiation is 96.6 cm^{-1}.

The coordinates of the platinum atom were found from a Patterson synthesis, and the other non-hydrogen atoms were located by subsequent difference-Fourier syntheses. Hydrogen atoms were fixed at calculated positions (C–H = 0.95 Å, $U(H) = 1.3U(C)$). The refinement of the scale factor, coordinates and anisotropic temperature factors of all non-non-hydrogen atoms converged to $R = 0.049$, $R_w = 0.057$, $w = 1/[\sigma(F_0)]^2$. The ratio of maximum least-squares shift to e.s.d. in the final refinement cycle

TABLE 1. Physical properties, yields and elemental analyses of $[NEt_4][PtLBr_3]$ complexes

Ligand	Melting point (°C)	Color	Yield (%)	Formula	Analysis: calc./found (%)		
					C	H	N
nsb	>200 dec.	yellow–orange	92	$C_{23}H_{29}Br_3ClN_3O_2SPt$	31.33 31.50	3.31 3.31	3.64[a] 3.55[a]
4-nsb	>220 dec.	orange	85	$C_{23}H_{29}Br_3ClN_3O_2SPt$	31.33 31.39	3.31 3.35	3.64[a] 3.70[a]
me-4-nsb	>190 dec.	dark orange	76	$C_{24}H_{31}Br_3ClN_3O_3SPt$	31.61 31.76	3.43 3.27	3.52[a] 3.57[a]
ohsb	>190 dec.	yellow–orange	85	$C_{23}H_{31}Br_3ClN_2OSPt$	33.76 33.84	3.82 3.85	3.92[a] 3.96[a]
asb	>210 dec.	orange	88	$C_{25}H_{33}Br_3ClN_2O_2SPt$	34.90 34.98	3.87 3.93	3.73[a] 3.77[a]
csb	>180 dec.	dark orange	95	$C_{23}H_{30}Br_3ClN_2SPt$	33.02 33.02	3.61 3.65	3.83[a] 4.11[a]
dmensb	>230 dec.	yellow–brown	78	$C_{25}H_{33}Br_3ClN_3O_4SPt$	31.88 31.78	3.10 3.10	3.40[a] 3.43[a]
nsbo	>180 dec.	dark orange	97	$C_{23}H_{29}Br_3ClN_3O_3Pt$	31.91 32.88	3.38 3.38	4.85 4.89
nsbse	>180 dec.	dark orange	91	$C_{23}H_{29}Br_3ClN_3O_2SePt$	29.75 29.86	3.15 3.20	4.52 4.50
cis-nsb	>175 dec.	orange	28	$C_{23}H_{29}Br_3ClN_3O_2SPt\cdot CH_3COCH_3$	33.23 33.00	3.75 3.62	4.47 4.90
nsbiz	>220 dec.	yellow	20	$C_{23}H_{30}Br_3ClN_4O_2Pt$	31.94 31.76	3.50 3.36	6.48 6.52
me-nsbiz	>170 dec.	yellow	97	$C_{24}H_{32}Br_3ClN_4O_2Pt$	32.80 32.65	3.67 3.75	6.37 6.33
et-nsbiz	>145 dec.	orange	89	$C_{25}H_{34}Br_3ClN_4O_2Pt$	33.63 33.63	3.84 3.37	6.27 6.21
ipr-nsbiz	135–140	orange	79	$C_{26}H_{36}Br_3ClN_4O_2Pt\cdot CH_3COCH_3$	36.09 36.96	4.39 4.41	
nbu-nsbiz	>170 dec.	dark orange	82				
bz-nsbiz	>190 dec.	dark orange	65	$C_{30}H_{36}Br_3ClN_4O_2Pt$	37.73 37.59	3.80 3.97	5.87 5.52
et-csbiz	>160 dec.	dark orange	92	$C_{25}H_{35}Br_3ClN_3Pt\cdot CH_3COCH_3$	37.12 37.20	4.56 4.69	

[a] Given as %S.

was <0.01. The last difference-Fourier synthesis showed a maximum electron density of 0.85 e Å^{3-} except for a few peaks near the Pt atom. The minimum was −0.49 e Å^{-3}.

$[NEt_4][Pt(me\text{-}4\text{-}nsb)Br_3]$

An orange crystal having approximate dimensions of 0.40 × 0.30 × 0.30 mm was mounted on a glass fiber with its long axis roughly parallel to the phi axis of the goniometer. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 24 reflections in the range $12 < \theta < 14°$. The complex crystallized in the monoclinic space group $P2_1/n$ with $Z = 4$. Cell parameters were $a = 10.729(6)$, $b = 23.554(6)$, $c = 12.294(7)$ Å, $\beta = 98.15(5)°$, $V = 3075(5)$ Å^3, $D_{calc} = 1.97$ g cm^{-3}. Systematic absences $0k0$ ($k = 2n + 1$), $h0l$ ($h + l = 2n + 1$); $+h, +k, \pm l$ with $h \leqslant 13$, $k \leqslant 29$, $|l| \leqslant 15$. A total of 6690 unique reflections were measured, 2922 with $F^2 > 2\sigma(F_0)^2$.

TABLE 2. Crystal data for $[NEt_4][PtLBr_3]$ complexes

	L = csb	L = me-4-nsb
Molecular weight (g/mol)	836.84	911.86
Space group	$P2_1/n$	$P2_1/n$
a (Å)	14.371(4)	10.729(6)
b (Å)	10.043(6)	23.554(6)
c (Å)	20.294(4)	12.294(7)
α (°)	90	90
β (°)	110.16(3)	98.15(5)
γ (°)	90	90
V (Å^3)	2750(4)	3075(5)
Z	4	4
F(000)	1592	1744
D_{calc} (g/cm^3)	2.02	1.97
μ(Mo Kα) (cm^{-1})	96.6	86.5
Transmission factor	0.403–0.999	0.571–0.999
$2\theta_{max}$ (°)	53	53
Scan technique	ω–θ	ω–θ
Unique reflections	5909	6690
Observed reflections	3288	2922
Refined parameters	280	319
R	0.049	0.057
R_w	0.057	0.068

Absorption corrections from psi-scans were applied and the relative transmission coefficients were found to range from 0.571 to 0.999. The linear absorption coefficient (μ) for this compound using Mo Kα radiation is 86.5 cm^{-1}.

The coordinates of the platinum atom were found from a Patterson synthesis, and the other non-hydrogen atoms were located by subsequent difference-Fourier syntheses. Hydrogen atoms were fixed at calculated postions (C–H = 0.95 N, U(H) = 1.3U(C)). The refinement of the scale factor, coordinates and anisotropic temperature factors of all non-hydrogen atoms converged to $R = 0.057$, $R_w = 0.068$, $w = 1/[\sigma(F_0)]^2$. The ratio of maximum least-squares shift to e.s.d. in the final refinement cycle was <0.02. The last difference-Fourier synthesis showed a few peaks (<1.22 e Å^{-3}) near the Pt atom.

Results and Discussion

All the complexes of the type $[NEt_4][Pt(L)Br_3]$ were obtained from the symmetric cleavage of the bromo-bridged binuclear complex $[NEt_4]_2[Pt_2Br_6]$ by the neutral ligand. In most of the cases the ligand was not completely soluble in the solvent used. However, it was found that the addition of the ligand as a suspension could be carried out without any complications. As the reaction proceeded, the ligand dissolved completely, as shown by the change in color of the reaction mixture. After about 30 min the desired product precipitated as powder in the reaction mixture. Attempts to recrystallize such powders, in order to obtain good crystals, were not successful. Suitable crystals were only obtained when the mother liquor was filtered and left to evaporate at room temperature.

Most of the complexes were obtained in excellent yields, about 80% average yield, except for the complexes with *cis*-nsb and nsbiz, which gave very low yields, 28 and 20% respectively (see Table 1). Heating and stirring for longer periods of time did not improve the yields for these reactions. The relatively low yields for these complexes may be due to the steric hindrance around the coordination center in the *cis*-nsb ligand and the low solubility of the nsbiz ligand. In general, reactions with styrylbenzothiazole derivatives were faster and gave better yields than reactions with the styrylbenzimidazole derivatives. No products were obtained when the reaction was carried out using a-nsb or cn-nsb as ligands. The structural formulas of these ligands **1**–**3** suggest that the N coordination centers in these ligands are probably too crowded to permit coordination of the ligand to the Pt atom.

The complexes were characterized by their melting points, elemental analyses, UV–Vis spectra and far-infrared spectra. The elemental analyses were satisfactory, even for cases in which only powders were obtained. During the initial stages of this study, the spectral data alone were not sufficient to assign with certainty the atom in the heterazole ligand which was coordinated. Thus, the crystal and molecular structures of several of these complexes were determined by X-ray diffraction techniques. Once the mode of coordination was established for those complexes as N-coordination in all cases, the spectra could be used to assign the remaining complexes.

Ultraviolet–Visible Spectra

The UV–Vis data for the complexes prepared in this work are summarized in Table 3. The spectra were taken in either CH_3CN or DMF as solvent, because most of the complexes were not completely soluble in other common solvents. These complexes are also soluble in DMSO, but use of this solvent was avoided, since the solvolysis of Pt(II) complexes in DMSO is relatively fast [20].

The anionic tribromo complexes show strong bands that are predominantly ligand absorptions, with molar absorptivities in the order of 10^4, as in the uncoordinated ligands. Also present are some strong bands in the region from 259–280 nm with ϵ 10^3 to 10^4, which were not observed in the free ligand and may be attributed to N–Pt charge transfer bands (LMCT). In the visible region very broad, weak bands (ϵ 65–341 cm^{-1} M^{-1}) occur, which were assigned as metal d–d electronic transitions. In some cases there was overlap of the metal d–d bands with ligand bands.

For the styrylbenzothiazole complexes the metal d–d absorptions range from 400–433 nm (ϵ 82–341

TABLE 3. UV–Vis spectral data for $[NEt_4][PtLBr_3]$ complexes

Ligand	Wavelength (nm) (ϵ)[a]
nsb	401(87), 333(2.53×10^4), 273.7(1.69×10^4), 261(1.75×10^4), 219(3.15×10^4) 403(9), 336.8(5.47×10^4), 269.2(3.32×10^4), taken in DMF
4-nsb	418(265), 360(6.71×10^4), 279.1(1.34×10^4), 221(1.63×10^4)
me-4-nsb	433(128), 366(1.39×10^4), 270(1.18×10^4), 209(9.86×10^3)
ohsb	418(111), 358.7(1.84×10^4), 307(9.48×10^3), 213(1.26×10^4) 402(10), 373(6.89×10^4), 262(9.20×10^3), taken in DMF
asb	415(82), 344.9(2.35×10^4), 210(1.48×10^4)
csb	419(98), 344(1.94×10^4), 206(1.19×10^4)
dmensb	412(341), 381(1.06×10^4), 265(9.55×10^3), 211(1.17×10^4)
nsbo	410(153), 326(1.47×10^4), 284(1.20×10^4), 204(1.83×10^4)
nsbse	404(209), 335(1.34×10^4), 265(1.10×10^4), 203(1.02×10^4)
cis-nsb	398(122), 273.7(1.78×10^4), 259.1(1.84×10^4), 219(3.26×10^4)
nsbiz	393(214), 332(2.99×10^4), 273.7(1.74×10^4), 259.4(2.41×10^4), 219(3.18×10^4)
me-nsbiz	390(214), 330(1.79×10^4), 262(1.25×10^4), 219(2.54×10^4)
et-nsbiz	395(65), 332(1.84×10^4), 284(1.83×10^4), 260(2.10×10^4), 220(2.97×10^4)
ipr-nsbiz	397(480), 384.3(7.64×10^3), 315(1.02×10^4), 258.1(1.20×10^4), 220(1.18×10^4)
nbu-nsbiz	403(94), 328.2(2.30×10^4), 273.7(1.25×10^4), 259.8(2.35×10^4), 219(3.20×10^4)
bz-nsbiz	395(161), 330.8(2.05×10^4), 259.2(2.05×10^4), 218(2.62×10^4)
et-csbiz	395(144), 325.0(1.76×10^4), 273.7(6.76×10^3), 259.7(1.24×10^4), 219(2.80×10^4) 384.3(251), 377.4(1.27×10^4), 362.9(1.27×10^4), 270.6(2.28×10^4), 221(2.64×10^4), taken in DMF

[a] All spectra were taken in CH_3CN as solvent, unless otherwise indicated.

TABLE 4. Far-infrared absorption bands for $[NEt_4][PtLBr_3]$ complexes

Ligand	Wavenumber (cm^{-1})	
	Pt–L	Pt–Br
nsb	456, 447, 432, 337, 324, 317	246, 232
4-nsb	478, 428	244, 225, 178
me-4-nsb	474, 435, 390	235, 228
ohsb	478, 430, 298	241, 238, 225, 142
asb	467, 435, 328, 324	243, 230, 228, 222, 194
csb	492, 488, 426, 323	243, 235, 225
dmensb	490, 476, 473, 417	238, 230, 236
nsbo	471, 455, 428	234, 227
nsbse	455, 408	239, 231, 226
cis-nsb	463, 451, 430	243, 232
nsbiz	437, 429	235, 219
me-nsbiz	436, 328, 324	247, 237, 234, 228, 219
et-nsbiz	477, 455, 430	247, 237, 228
ipr-nsbiz	470, 433, 366	235, 218
nbu-nsbiz	494, 439	240, 233
bz-nsbiz	464, 436, 386, 326	240, 225
et-csbiz	454, 442, 438, 320	236

cm^{-1} M^{-1}), whereas the styrylbenzimidazole derivatives show metal d–d absorptions in a slightly lower wavelength range, 390–403 nm, ϵ 65–214 cm^{-1} M^{-1}. The complex with me-4-nsb has the highest value of λ_{max}, 433 nm, and has been shown by X-ray structural determination (*vide infra*) to have Pt–N coordination and not Pt–S coordination. Thus, all the complexes were assigned as Pt–N coordinated.

Far-infrared Spectra

The far-infrared spectra of the tribromo anionic complexes can be divided into two regions: Pt–L stretching with ν between 500 and 300 cm^{-1}, and Pt–Br stretching, with $\nu < 250$ cm^{-1}. These are listed in Table 4. The assignment of the Pt–Br stretching vibrations was based on their high intensity and characteristic frequency [21]. There are at least two strong Pt–Br stretching bands. In some cases the Pt–Br vibrations are split and three or more bands are observed, indicating that mixing of some vibrational modes has occurred. No attempts were made to assign these Pt–Br vibrations as P–Br *cis* or *trans* to L vibrations, due to the large range in which these bands appear.

Pt–L stretching vibrations appear in the higher frequency region of the spectra (from 300 to 500 cm^{-1}) with low intensities, which is characteristic of either Pt–N or Pt–S vibrations [22]. It was impossible using the frequencies alone to decide whether they resulted from Pt–N or Pt–S coordination. However, since Pt–N vibrations generally have higher frequencies than Pt–S vibrations [22], and since X-ray structural studies (*vide infra*) have shown that four different styrylbenzothiazole derivatives are bound to Pt through the N and not the S atom, the Pt–L bands can be assigned with some confidence as Pt–N vibrations.

X-ray Diffraction Studies

Structure of [NEt$_4$][Pt(csb)Br$_3$]

The atomic coordinates and isotropic thermal parameters are listed in Table 5. An ORTEP plot [23] of the title compound with the atom numbering is shown in Fig. 1, and the packing of the molecules [24] in Fig. 2. Selected bond lengths and angles are in Table 6.

TABLE 5. Atomic coordinates and equivalent isotropic temperature factors (Å^2) for [NEt$_4$][Pt(csb)Br$_3$]

Atom	x	y	z	B (Å^2)
Pt	0.71359(3)	0.30052(5)	0.42682(2)	3.407(9)
Br1	0.6121(1)	0.4717(2)	0.35239(8)	5.75(4)
Br2	0.8390(1)	0.3253(2)	0.37331(8)	6.82(4)
Br3	0.8094(1)	0.1333(2)	0.50730(9)	6.80(4)
Cl	0.6399(3)	0.6501(4)	0.7393(2)	6.4(1)
S	0.4986(2)	0.3004(4)	0.5457(2)	4.29(7)
N1	0.6064(7)	0.274(1)	0.4691(5)	3.9(2)
N2	0.6342(8)	0.297(1)	0.1350(5)	4.9(3)
C1	0.5259(7)	0.192(1)	0.4392(6)	3.5(3)
C2	0.5127(9)	0.108(1)	0.3830(6)	4.2(3)
C3	0.4295(9)	0.028(1)	0.3615(7)	4.8(3)
C4	0.3614(9)	0.030(1)	0.3971(7)	5.1(4)
C5	0.3772(9)	0.110(1)	0.4556(7)	5.0(3)
C6	0.4594(8)	0.191(1)	0.4755(6)	3.5(3)
C7	0.6017(8)	0.341(1)	0.5252(5)	3.2(2)
C8	0.6784(8)	0.431(1)	0.5652(6)	3.7(3)
C9	0.6719(8)	0.506(1)	0.6158(6)	3.6(3)
C10	0.7504(9)	0.599(1)	0.6590(6)	3.9(3)
C11	0.7416(9)	0.673(1)	0.7143(6)	4.3(3)
C12	0.812(1)	0.759(1)	0.7508(7)	5.3(4)
C13	0.899(1)	0.733(1)	0.7360(7)	5.7(4)
C14	0.911(1)	0.702(2)	0.6832(8)	6.8(4)
C15	0.8381(9)	0.614(1)	0.6444(6)	5.6(3)
C16	0.739(1)	0.251(2)	0.169(1)	9.7(6)
C17	0.815(1)	0.341(2)	0.156(1)	12.2(8)
C18	0.629(1)	0.425(2)	0.1722(9)	7.9(5)
C19	0.528(1)	0.488(2)	0.150(1)	8.8(5)
C20	0.566(1)	0.194(2)	0.152(1)	8.7(6)
C21	0.579(2)	0.159(2)	0.2207(9)	12.6(7)
C22	0.605(1)	0.328(2)	0.0590(8)	9.0(6)
C23	0.624(2)	0.196(2)	0.018(1)	12.8(7)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

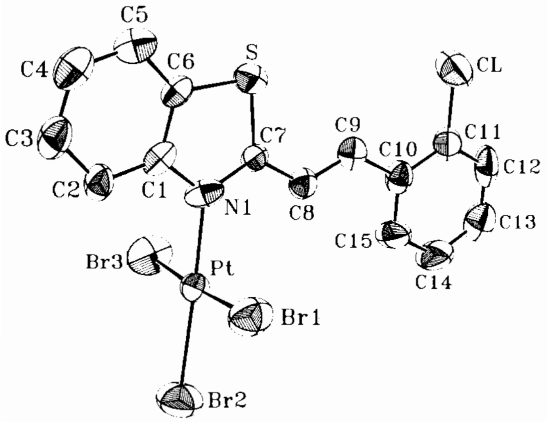

Fig. 1. Labeling of atoms in the $[Pt(csb)Br_3]^-$ anion (50% probability ellipsoids).

The crystal structure consists of $[Pt(csb)Br_3]^-$ anions and $[NEt_4]^+$ cations packed in a monoclinic unit cell which contains four formula units. The $[Pt(csb)Br_3]^-$ unit has square planar geometry about the Pt with no atom deviating from the least-squares coordination plane by more than 0.05(1) Å. The csb molecule is coordinated to the Pt through the N of the benzothiazole ring. The Pt–N and average Pt–Br bond distances are 2.02(1) and 2.417(2) Å, respectively.

The csb molecule is essentially planar with a dihedral angle of only 6.7(2)° between the benzothiazole and the chlorobenzene rings. This result contrasts with the structures previously reported [14–16] in which the styrylbenzothiazole ligands

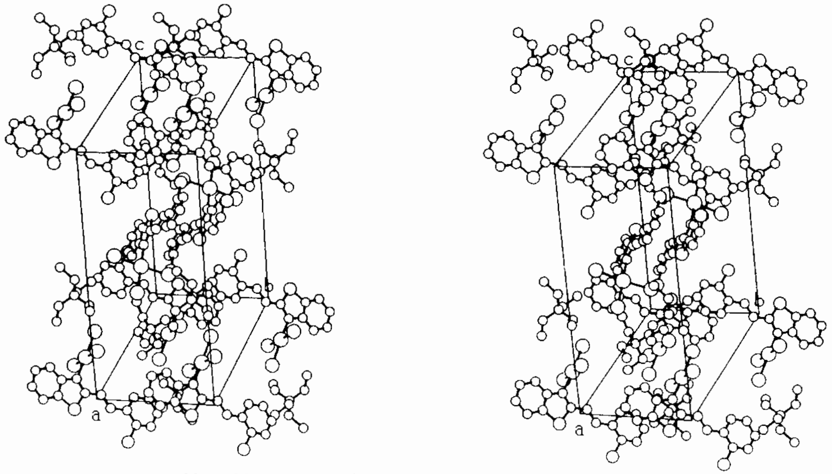

Fig. 2. Packing of $[NEt_4][Pt(csb)Br_3]$ ions in the unit cell.

TABLE 6. Selected bond distances (Å) and angles (°) in $[NEt_4][Pt(csb)Br_3]$

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Atom 3	Angle
Pt	Br1	2.418(1)	Br1	Pt	Br2	91.66(6)
Pt	Br2	2.417(2)	Br1	Pt	Br3	175.88(7)
Pt	Br3	2.415(2)	Br1	Pt	N1	88.6(2)
Pt	N1	2.02(1)	Br2	Pt	Br3	92.05(6)
N1	C1	1.38(1)	Br2	Pt	N1	177.8(3)
N1	C7	1.34(1)	Br3	Pt	N1	87.8(3)
S	C6	1.73(1)	Pt	N1	C1	122.6(9)
S	C7	1.72(1)	Pt	N1	C7	124.2(8)
Cl	C11	1.72(1)	C6	S	C7	90.7(6)
N2	C (ethyl)	1.51(2) (av.)	C1	N1	C7	113(1)
C	C (bzthzl phenyl)	1.39(2) (av.)	C	N2	C (av.)	105(1)
C	C (styryl phenyl)	1.38(2) (av.)	C	C	C (bzthzl av.)	122(2)
			C	C	C (styryl phenyl av.)	120(1)
C7	C8	1.44(1)	S	C7	N1	112.8(8)
C8	C9	1.30(2)	S	C6	C1	110.1(8)
C9	C10	1.49(1)	N1	C1	C6	113(1)
			S	C7	C8	124.5(9)
			N1	C7	C8	123(1)
			C7	C8	C9	124(1)
			C8	C9	C10	125(1)

were found to be non-planar. From the packing diagram of the present complex it can be seen that there are no π-stacking interactions between the aromatic rings of the ligand molecules.

The average C–N, C–S and C–C distances (1.36(3), 1.73(1), 1.39(1) Å) and C–C–C angles (120(2)°) for the coordinated csb ligand are all normal and in agreement with those found in the previous analogues. The benzothiazole and chlorobenzene rings are essentially planar with no atom deviating from the least-squares planes by more than 0.04(1) Å. The dihedral angles between the $PtNBr_3$ plane and the benzothiazole and chlorobenzene planes are 92.1(1) and 91.7(2)°, respectively. The distances and angles within the tetraethylammonium cation are all normal.

Structure of [NEt_4][Pt(me-4-nsb)Br_3]

The atomic coordinates and the thermal parameters are listed in Table 7. An ORTEP plot [23] with the atom numbering is shown in Fig. 3 and the packing of the molecules [24] in Fig. 4. Selected bond lengths and angles are in Table 8.

The $[Pt(me\text{-}4\text{-}nsb)Br_3]^-$ anions and $[NEt_4]^+$ cations are packed in a monoclinic unit cell which contains four formula units. The $[Pt(me\text{-}4\text{-}nsb)Br_3]^-$ unit has square planar coordination about the Pt with the maximum deviation from the least-squares coordination plane of 0.004(1) Å. As in the previous complex, the me-4-nsb molecule is coordinated to the Pt through the N of the benzothiazole ring. The Pt–N and average Pt–Br bond distances are 2.03(2) and 2.416(7) Å, respectively.

TABLE 7. Atomic coordinates and equivalent isotropic temperature factors ($Å^2$) for $[NEt_4][Pt(me\text{-}4\text{-}nsb)Br_3]$

Atom	x	y	z	B ($Å^2$)
Pt	0.05881(7)	0.18465(3)	0.06637(6)	3.41(1)
Br1	−0.0564(2)	0.13594(9)	0.1945(2)	5.96(6)
Br2	0.0489(2)	0.27415(9)	0.1604(2)	5.71(6)
Br3	0.1749(2)	0.2286(1)	−0.0651(2)	6.22(6)
Cl	0.5425(6)	−0.0542(2)	0.1541(6)	7.0(2)
S	0.1465(5)	0.0131(2)	−0.0715(4)	4.6(1)
O1	−0.265(1)	0.0230(5)	−0.351(1)	5.5(4)
O2	0.892(2)	0.0431(8)	0.422(1)	9.0(5)
O3	0.810(2)	0.1184(8)	0.486(1)	10.3(6)
N1	0.070(1)	0.1103(7)	−0.015(1)	4.2(4)
N2	0.806(2)	0.0764(8)	0.425(1)	7.0(5)
N3	0.616(1)	0.2757(5)	0.052(1)	3.1(3)
C1	−0.019(2)	0.0924(7)	−0.101(1)	3.2(4)
C2	−0.129(2)	0.1209(7)	−0.146(1)	3.7(4)
C3	−0.207(2)	0.0957(8)	−0.229(1)	4.5(5)
C4	−0.176(2)	0.0418(7)	−0.270(1)	4.5(5)
C5	−0.070(2)	0.0143(7)	−0.227(2)	4.0(4)
C6	0.009(2)	0.0396(7)	−0.144(1)	3.8(4)
C7	0.163(1)	0.0728(7)	0.010(1)	3.4(4)
C8	0.270(2)	0.0823(8)	0.092(1)	4.3(5)
C9	0.354(2)	0.0426(8)	0.122(1)	4.2(5)
C10	0.471(2)	0.0526(8)	0.202(2)	4.7(5)
C11	0.561(2)	0.0093(7)	0.223(2)	4.3(5)
C12	0.671(2)	0.0190(8)	0.292(2)	4.2(5)
C13	0.688(2)	0.0682(8)	0.351(2)	5.8(6)
C14	0.601(2)	0.1113(8)	0.337(2)	6.3(6)
C15	0.491(2)	0.1031(9)	0.263(2)	5.8(6)
C16	−0.241(2)	−0.031(1)	−0.396(2)	7.0(7)
C17	0.480(2)	0.275(1)	0.063(2)	8.4(8)
C18	0.442(2)	0.256(1)	0.171(2)	6.4(6)
C19	0.689(3)	0.311(1)	0.141(2)	9.2(9)
C20	0.654(3)	0.3731(8)	0.135(2)	10.0(9)
C21	0.672(3)	0.218(1)	0.069(2)	10.4(9)
C22	0.591(3)	0.176(1)	−0.008(2)	10.0(9)
C23	0.629(3)	0.298(1)	−0.057(2)	10.1(9)
C24	0.766(2)	0.296(1)	−0.085(2)	8.5(8)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

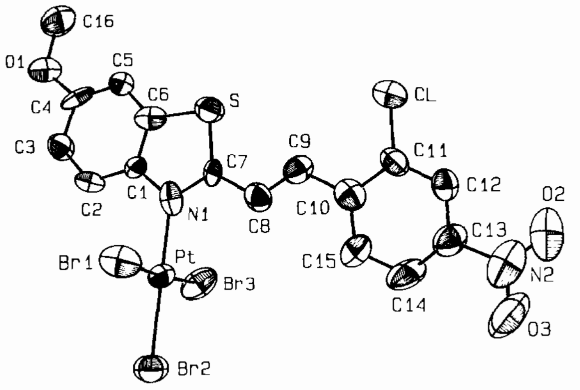

Fig. 3. Labeling of atoms in the $[Pt(me\text{-}4\text{-}nsb)Br_3]^-$ anion (50% probability ellipsoids.

The me-4-nsb molecule is essentially planar with a dihedral angle of 6(4)° between the benzothiazole and the nitrobenzene rings. This result is similar to that found in the $[NEt_4][Pt(csb)Br_3]$ structure just discussed. From the packing diagram of the present complex it can be seen that there are no π-stacking interactions between the aromatic rings of the ligand molecules.

The average C–N, C–S and C–C distances (1.37(4), 1.73(1), 1.38(3) Å) and C–C–C angles (120(1)° for the coordinated me-4-nsb ligand are all normal and agree with those found in previously discussed analogues. The benzothiazole and nitrobenzene rings are essentially planar with no atom deviating from the least-squares planes by more than 0.03(2) Å. The dihedral angles between the $PtNBr_3$ plane and the benzothiazole and nitrobenzene planes are 89.8(2) and 86.0(4)°, respectively.

This compound gave $R = 0.057$, which is higher than the R value obtained for the other related structures. This probably resulted from disorder in the tetraethylammonium cation, where the positions of some of the methyl carbons did not refine well.

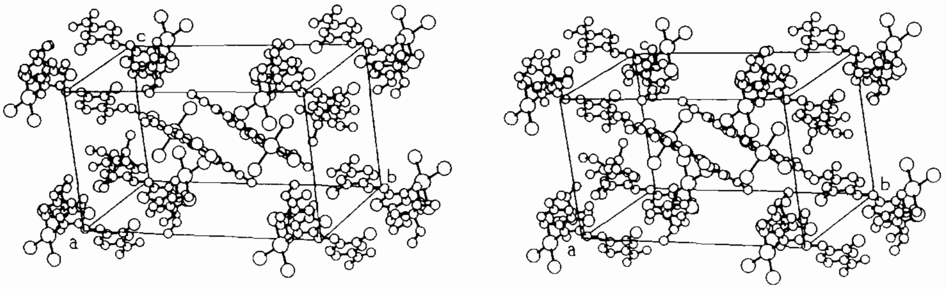

Fig. 4. Packing of $[NEt_4][Pt(me\text{-}4\text{-}nsb)Br_3]$ ions in the unit cell.

TABLE 8. Selected bond distances (Å) and angles (°) in $[NEt_4][Pt(me\text{-}4\text{-}nsb)Br_3]$

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Atom 3	Angle
Pt	Br1	2.424(3)	Br1	Pt	Br2	92.35(8)
Pt	Br2	2.414(2)	Br1	Pt	Br3	177.14(9)
Pt	Br3	2.410(3)	Br1	Pt	N1	89.2(5)
Pt	N1	2.03(2)	Br2	Pt	Br3	90.50(9)
N1	C1	1.39(2)	Br2	Pt	N1	178.5(5)
N1	C7	1.34(2)	Br3	Pt	N1	88.0(4)
S	C6	1.73(2)	Pt	N1	C1	124(1)
S	C7	1.72(2)	Pt	N1	C7	124(1)
Cl	C11	1.72(2)	C6	S	C7	91.1(7)
O1	C4	1.36(2)	C1	N1	C7	113(1)
O1	C16	1.42(3)	C4	O1	C16	116(2)
O2	N2	1.21(3)	C	C	C (bzthzl phenyl)	120(2) (av.)
O3	N2	1.24(3)	C	C	C (styryl phenyl)	120(2) (av.)
N2	C13	1.47(3)	S	C6	C1	110(1)
N3	C (ethyl)	1.49(3) (av.)	N1	C1	C6	113(1)
C	C (bzthzl phenyl)	1.38(2) (av.)	S	C7	N1	113(1)
C	C (styryl phenyl)	1.39(3) (av.)	S	C7	C8	123(1)
			N1	C7	C8	124(2)
C7	C8	1.43(2)	O2	N2	O3	125(2)
C8	C9	1.32(3)	C7	C8	C9	122(2)
C9	C10	1.49(3)	C8	C9	C10	123(2)

TABLE 9. Selected bond lengths (A) and angles (°) for *cis*-Pt(asb)$_2$Cl$_2$ and [NEt$_4$][PtLBr$_3$] complexes

	cis(asb)$_2$	asb	csb	me-4-nsb	nsb^b
<Pt–Br>	2.287(5)^a	2.426(7)	2.417(2)	2.416(7)	2.431(7)
Pt–N	2.035(1)	2.010(8)	2.02(1)	2.03(2)	2.01(1)
N1–C1	1.407(6)	1.39(1)	1.38(1)	1.39(2)	1.38(1)
N1–C7	1.320(4)	1.33(1)	1.34(1)	1.34(2)	1.32(2)
S–C6	1.736(8)	1.71(1)	1.73(1)	1.73(2)	1.74(1)
S–C7	1.728(5)	1.718(9)	1.72(1)	1.72(2)	1.72(2)
C1–N1–C7	112(1)	110.7(7)	113(1)	113(1)	111(1)
C6–S–C7	90.1(1)	89.9(5)	90.7(6)	91.1(7)	89.6(7)
Dihedral angles (°)^c					
PtBr$_3$–bzthzl	80.37(8) 75.07(8)	85.7(1)	92.1(1)	89.8(2)	73.9(2)
PtBr$_3$–benzene	64.4(1) 74.0(1)	71.3(3)	91.7(2)	86.0(4)	79.3(3)
bzthzl–benzene	33.4(3) 38.4(1)	22.4(7)	6.7(2)	6(4)	60.1(4)

[a] <Pt–Cl> bond length. [b] Data taken from ref. 14. [c] PtBr$_3$ = coordination plane; bzthzl = benzothiazole plane; benzene = styryl benzene.

General Remarks about the Structures

Some general remarks can be made about the structures of these compounds. A summary of similarities and differences is given in Table 9. The csb and me-4-nsb ligands are ambidentate with either the N or the S atom available for coordination. Since Pt(II) is a soft acid, coordination through S rather than through N might be expected [25]. However, from the structural data, it is evident that the ligands are coordinated through the N of the benzothiazole ring. The angle at the S atom in the thiazole rings is always much smaller (near 90°) than the angle at the N atom. This suggests that the S atom might be using unhybridized p orbitals for bonding.

No clear evidence for any *trans* influence could be noted in the Pt–Br distances. In similar structures the Pt–N bond distance which is *trans* to the Br atom varies from 1.96(1) Å, for an acetonitrile complex [26], to 2.01(1) Å for the nsb complex [14]. However, in a diethylenetriamine Pt(II) complex [27] the Pt–N bond distance ranges from 1.95(5) to 2.08(5) Å, with the Pt–N distance which is *trans* to the Br atom being the shortest one.

The major difference among the structures studied is in the degree of planarity of the coordinated ligand. Possible factors which might contribute to this deviation from planarity include: (i) loss of aromaticity through ligand coordination; (ii) electronic repulsions between the H atoms of C8 and benzene ring; (iii) packing of the molecules in the unit cell. In both *cis*-Pt(asb)$_2$Cl$_2$ and [NEt$_4$][Pt(asb)Br$_3$] the asb molecules are non-planar with dihedral angles of 33.4(3) and 38.3(2)° in the former and 22.4(7)° in the latter. However, the csb and me-4-nsb ligands are almost planar with dihedral angles of 6.7(2) and 6(4)°; respectively. In the related [NEt$_4$][Pt(nsb)Br$_3$] complex a dihedral angle of 60.1(4)° was observed. Since there is no clear structural–planarity relationship, it seems, then, that the deviation from planarity in these complexes can be attributed principally to packing forces. Related uncoordinated styrylbenzothiazole derivatives are planar in the crystalline state [28].

Although the average C–N and C–S distances, 1.36(3) and 1.73(1) Å, for the coordinated benzothiazole are similar among the analogous complexes, the average C–N and C–S distances for two uncoordinated styrylbenzothiazole derivatives are 1.34(5) and 1.74(1) Å [28]. It is evident that upon coordination the <C–N> distance increases by 0.02 Å while the <C–S> distance decreases by 0.01 Å. These changes can be attributed to a strong σ Pt–N interaction.

Conclusions

Seventeen Pt(II) complexes of the type [NEt$_4$]-[Pt(L)Br$_3$] with styrylbenzoheterazole derivatives were synthesized and characterized by elemental analyses, melting points, UV–Vis and far-IR spectra. The crystal and molecular structures of some of the complexes were determined by X-ray diffraction techniques. The styrylbenzothiazole ligands with either the N or the S atom available for coordination were coordinated to Pt through the N atom, not the S atom. The degree of planarity of the coordinated ligands varied and dependend principally on the packing forces.

Supplementary Material

Lists of structure factors, anisotropic thermal factors, H-atom coordinates and least-squares planes information are available from author M. M. Muir on request.

Acknowledgements

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