Synthesis and Characterization of New Platinum(II) Complexes Containing Thiazole and Imidazole Donors†

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Abstract

A number of new complexes of Pt(II) of the type *cis*-$Pt(NH_3)(L)Cl_2$, where L = thiazole (Tz), 2-bromothiazole (2-Brt), benzothiazole (Bt), 2,1,3-benzothiadiazole (213-Btd), 1,2,3-benzothiadiazole (123-Btd), imidazole (Iz) and 1-methylimidazole (N-Miz) have been prepared. The complexes were characterized by infrared and UV–Vis spectroscopy, proton NMR and elemental analyses. The thiazoles and benzothiazoles were coordinated through the nitrogen heteroatom. However, both the benzothiadiazoles were coordinated through the sulfur heteroatom. Several of the complexes showed significant cytotoxic activity.

Introduction

Complexes of the type *cis*-PtA_2Cl_2, where A is NH_3 or amine, are of considerable interest as known or potential antitumor agents [1]. Variations in the nature of the amine can have a significant effect on the activity and toxicity of the complex. There have not, however, been many studies using other types of ligands or mixed ligand systems, although there would seem to be possibilities of improving antitumor activity or reducing toxicity by combining different ligands in one complex [2]. In an attempt to understand better the role of the amine ligands, a series of mixed ligand complexes of the type *cis*-$Pt(NH_3)(L)Cl_2$ has been prepared. The ligands L included thiazole (Tz), 2-bromothiazole (2-Brt), benzothiazole (Bt), 2,1,3-benzothiadiazole (213-Btd), 1,2,3-benzothiadiazole (123-Btd), imidazole (Iz) and 1-methylimidazole (N-Miz). These systems are of interest for several reasons: imidazole [3], thiazole and benzothiazole derivatives [4] are known to be biologically active, so their complexes should be of interest. The complexes *cis*-$Pt(L)_2Cl_2$ where L = Iz [5, 6], N-Miz [7] and Bt [8], have been studied as potential antitumor drugs. The sulfur heteroatom in some of the ligands is a potential coordination center which might provide information about the role of a ligand with a higher *trans* effect than ligands with N-coordination.

Experimental

Physical Methods

Infrared spectra were recorded using a Nicolet 6000 Series 80 FTIR spectrophotometer or a Perkin-Elmer 599 IR spectrophotometer. The complexes were sampled as KBr pellets or as Nujol mulls between KBr cells. For the region below 500 cm^{-1} Nujol mulls between polyethylene discs were used. ^{13}C NMR spectra were recorded using a JEOL FX-90Q NMR spectrometer. ^1H NMR spectra were obtained with either the JEOL FX-90Q or a Varian T-60 NMR spectrometer, using tetramethylsilane as external standard.

UV–Vis spectra were recorded using a Hitachi–Perkin-Elmer 200 or a Perkin-Elmer 139 spectrophotometer. Melting points are uncorrected and were measured in capillary tubes using a Thomas Hoover capillary melting point apparatus. Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, Ga.

Cytotoxicity Tests

The screening of compounds for cytotoxic activity was performed following the protocol for *in vitro* KB cell culture screen NCI, Monograph 150, and has been described elsewhere [9]. Complexes were dissolved in DMSO and enough water was added to make the solution 1% in DMSO.

Starting Materials

The ligands Tz, Brtz, Iz and N-Miz were purchased from Aldrich Chemical Corporation; Bt, 123-Btd and 213-Btd were purchased from Fluka

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A.G., and K_2PtCl_4 from Strem Chemical Company. $[Pt(NH_3)_4]Cl_2$ was prepared by the standard method [10] and *cis*-$Pt(NH_3)_2Cl_2$ by the method of Lebedinskii and Golovnya [11]. $K[Pt(NH_3)Cl_3$ was prepared according to Elleman *et al.* [12]. *cis*-$Pt(NH_3)_2Cl_2$ (1.5 g, 5.0 mmol) was refluxed for 2 h in concentrated HCl (50 ml) with 0.1 g of Pt powder as catalyst. After removing unreacted complex and catalyst, the $[Pt(NH_3)Cl_3]^-$ ion was precipitated as the golden salt $[Pt(NH_3)_4][Pt(NH_3)Cl_3]_2$ by addition of an excess of a concentrated solution of $[Pt(NH_3)_4]Cl_2$. The golden salt was filtered and washed several times with water, followed by ethanol and ether to give 1.3 g (1.4 mmol) of $[Pt(NH_3)_4]$-$[Pt(NH_3)Cl_3]_2$. This solid was suspended in 2 ml water and 3 ml of an aqueous solution containing 0.6 g (1.4 mmol) of $K_2[PtCl_4]$ was added. The mixture was heated until the golden salt seemed to be completely converted to the green salt $[Pt(NH_3)_4][PtCl_4]$ and aqueous $[Pt(NH_3)Cl_3]^-$. The insoluble salt was removed and the yellow–orange filtrate was evaporated in air to give 0.9 g of $K[Pt(NH_3)Cl_3]$.

Syntheses of New Complexes

Synthesis of cis-dichloroamminethiazoleplatinum(II): general procedure for mixed ligand systems

A solution of thiazole (42 μl, 0.6 mmol) in 2 ml of a 2:1 H_2O:EtOH mixture was mixed with 3 ml of aqueous $K[Pt(NH_3)Cl_3]$ (0.21 g, 0.6 mmol) with stirring. A pale yellow solid began to precipitate, but stirring was continued for 12 h. The solution was filtered and the yellow solid was washed with water, ethanol and ether to give 0.1 g of *cis*-$Pt(NH_3)(Tz)Cl_2$ (45% yield), melting point (m.p.) 153–154 °C.

cis-dichloroamminebenzothiazoleplatinum(II)

Following the general procedure, this compound was obtained as a pale yellow solid (m.p. 160 °C) in 62% yield from $K[Pt(NH_3)Cl_3]$ (0.21 g, 0.6 mmol) and benzothiazole (63 μl, 0.6 mmol).

cis-Dichloroammine(2-bromothiazole)platinum(II)

Following the general procedure, the compound was obtained as a brownish yellow solid in 30% yield from $K[Pt(NH_3)Cl_3]$ (0.23 g, 0.65 mmol) and 2-bromothiazole (60 μl, 0.65 mmol), m.p. 170 °C (dec).

cis-Dichloroammine(2,1,3-benzothiadiazole)platinum(II)

Following the general procedure, this compound was obtained as a bright yellow solid in 75% yield from $K[Pt(NH_3)Cl_3]$ (0.16 g, 0.45 mmol) and 2,1,3-benzothiadiazole (0.62 g, 0.45 mmol). The compound did not melt below 200 °C.

cis-Dichloroammine(1,2,3-benzothiadiazole)platinum(II)

This compound was obtained as a bright orange solid in 45% yield from $K[Pt(NH_3)Cl_3]$ (0.078 g, 0.22 mmol) and 1,2,3-benzothiadiazole (0.030 g, 0.22 mmol) according to the general procedure. The compound decomposed at 170 °C.

cis-Dichloroammine(N-methylimidazole)platinum(II)

Twenty ml of an aqueous solution of $K[Pt(NH_3)Cl_3]$ (0.6 g, 1.7 mmol) were mixed with 5 ml of an aqueous solution of *N*-methylimidazole (134 μl, 1.7 mmol). The reaction mixture was quickly filtered to remove the solid which precipitated. The mixed ligand complex was obtained in 17% yield, m.p. 194 °C.

cis-Dichloroammineimidazoleplatinum(II)

Two ml of an aqueous solution of $K[Pt(NH_3)Cl_3]$ (0.24 g, 0.65 mmol) were mixed with 2 ml of a solution of imidazole (0.045 g, 0.65 mmol). The solution of the ligand was previously neutralized by the dropwise addition of 2 M HCl. The product was obtained as a brownish-yellow solid in 7% yield from $K[Pt(NH_3)Cl_3]$ and imidazole. The m.p. was greater than 200 °C.

Results and Discussion

The synthesis of the mixed ammine–ligand systems of platinum(II) with two chloride groups in the *cis* positions requires the use of the trichloroammineplatinate(II) ion in a substitution reaction with the desired ligand. The *trans* effect ensures that the chloride *cis* to the NH_3 group is replaced to give the corresponding *cis*-isomer. Confirmation of the structures of this series of complexes rests on satisfactory elemental analyses, ^1H NMR, UV–Vis and IR spectral data.

The preparation of mixed ammine–ligand complexes of platinum(II) was attempted for several ligands having the thiazole or imidazole moiety. The complexes precipitated as powders on reaction of the ligands with an aqueous solution of $K[Pt(NH_3)Cl_3]$. Attempted reactions of this starting complex with aliphatic amines such as cyclohexylamine gave decomposition, which was readily observed as pronounced darkening of the reaction mixture. Reaction mixtures for most thiazole systems did not tend to darken over a period of hours. The syntheses with imidazole and *N*-methylimidazole could be performed with weakly acid to neutral solutions of the ligand, although dark solids always eventually formed. The relatively low yields for these ligands are indicative of the difficulties encountered in their syntheses. Elemental analyses were carried out for

TABLE I. Elemental Analyses for *cis*-$Pt(NH_3)(L)Cl_2$

L	Formula	Analysis: calc. (found) (%)			
		C	H	N	S
Tz	$C_3H_6Cl_2N_2SPt \cdot \frac{1}{3}C_2H_5OH$	11.48	2.10	8.38	7.20
		(11.50)	(1.67)	(8.33)	(7.27)
Bt	$C_7H_8Cl_2N_2SPt \cdot \frac{1}{2}C_2H_5OH$	21.77	2.51	7.27	6.35
		(21.60)	(2.24)	(7.20)	(6.23)
2-Brt	$C_3H_5BrCl_2N_2SPt \cdot \frac{1}{4}C_2H_5OH$	9.17	1.43	6.11	6.98
		(9.04)	(1.29)	(5.93)	(6.90)
213-Bdt	$C_6H_7Cl_2N_3SPt$	17.19	1.68	10.02	7.67
		(17.46)	(1.80)	(9.98)	(7.72)
123-Bdt	$C_6H_7Cl_2N_3SPt$	17.19	1.68	10.02	a
		(17.40)	(1.72)	(10.16)	(a)
N-Miz	$C_4H_9Cl_2N_3Pt$	13.16	2.48	11.50	b
		(13.60)	(2.63)	(11.13)	(b)
Iz	$C_3H_7Cl_2N_3Pt$	10.26	2.01	11.97	c
		(10.56)	(2.14)	(11.53)	(c)

[a]% Cl Calc. = 16.91; Found = 17.17. [b]% Cl Calc. = 19.42; Found = 19.02. [c]% Cl Calc. = 20.20; Found = 19.96.

TABLE II. Proton NMR Chemical Shifts for Free Ligands and the Corresponding *cis*-$Pt(NH_3)(L)Cl_2$ Complexes

Compound	Chemical shifts (ppm)
Tz	8.9, 7.7, 7.5
Complex	9.5, 7.9, 7.8
Bt	7.3, 7.4, 7.8, 8.1, 8.9
Complex	7.4, 7.5, 8.0, 8.7, 9.7
2-Brt	7.6, 7.3
Complex	7.7, 7.6
213-Btd	7.6, 7.8
Complex	solvent substitution
123-Btd	7.6, 7.7, 8.2, 8.5
Complex	solvent substitution
N-Miz	3.6, 6.7, 6.9, 7.5
Complex	3.2, 6.8, 7.2, 8.2
Iz	7.0, 7.6
Complex	7.1, 6.8, 8.0

all reported mixed ammine–ligand complexes and are compiled in Table I.

NMR Spectral Data

In all cases proton magnetic resonance shows the presence of coordinated ligands as shown by their corresponding hydrogen resonances (see Table II). The presence of the characteristic NH_3 unsymmetrical broad band in the range 3.6–4.6 ppm was observed in all cases, confirming the mixed ligand nature of the complexes. The assignments of ring proton resonances in the spectra of the free ligands were found in the literature [13]. The spectral assignments of the complexes were based on comparison with the shapes and positions in the corresponding spectra of the pure ligands. Almost all signals are shifted upon complexation, as the result of the electric field effect caused by complexation, π-bonding and temperature-independent paramagnetism of the platinum ion [14].

The signals of the H(2) resonances show the largest shifts upon complexation. Values of $\Delta\nu$ (ppm) for H(2) for the Tz, Bt, N-Miz and Iz systems were 0.6, 0.8, 0.7 and 0.4, respectively. Less pronounced downfield shifts, from 0.1–0.3 ppm, were observed for protons on carbon atoms adjacent to the sulfur and nitrogen heteroatoms in the Tz and 2-Brt complexes. The benzothiazole system is more complicated and assignments were made only for the proton on C(2). For *N*-methylimidazole, the relative magnitudes of the shifts in proton resonances follow the order C(2) > C(4) > C(5).

The ^1H NMR spectrum of *cis*-$Pt(NH_3)(Tz)Cl_2$ showed two satellites with $^3J(^{195}Pt-^1H) = 35$ Hz for the H(2) resonance. The *cis*-$Pt(NH_3)(Bz)Cl_2$ complex shows satellites for the H(2) resonance with $^3J(^{195}Pt-^1H) = 50$ Hz. No coupling could be observed for imidazole complexes due to the low resolution of their spectra.

Coupling constants between the ring protons and ^{195}Pt in *cis*-$Pt(NH_3)(L)Cl_2$ complexes can be compared to values reported for other heterocyclic aromatic rings. The coupling of ^{195}Pt with the H(2) proton in a benzimidazole complex is 22.5 Hz and in an *N*-methylimidazole complex is 22 Hz [7]. In addition, Kong and Theophanides [15] found that platinum–purine nucleoside complexes have coupling constants of 26 Hz for the proton at C(8) with ^{195}Pt coordinated at the N(7) atom. It is interesting that there is a difference of about 25 Hz between the coupling constant

for the benzimidazole system and that reported in this work for benzothiazole.

^{13}C NMR spectra were expected to confirm or give more information about possible sites of coordination. However, the use of DMSO as solvent complicated the interpretation of the spectral data, since gradual coordination of the solvent was observed. This is known for other Pt(II) complexes [16, 17]. The reaction was sufficiently slow for the ^1H spectral results to be useful.

Infrared Spectral Data

The infrared spectral data summarized in Table III for all the complexes show the absorptions due to the heterocyclic ligand vibrations and to NH_3, thus confirming the presence of both in the complex. Degenerate and symmetric stretching modes of NH_3 can be unambiguously assigned in mixed ligand complexes, since they do not overlap with vibrations due to the L groups. They appear in the region of 3280 ± 20 cm^{-1} and 3190 ± 10 cm^{-1} for almost all the complexes.

TABLE III. Infrared Absorption Bands for *cis*-$Pt(NH_3)(L)Cl_2$[a]

L	$\bar{\nu}$ (cm^{-1})
Tz	1619, 1506, 1389, 1305, 1064, 882, 813, 449, 327, *325, 321,* 260
Bt	1610, 1565, 1468, 1450, 1415, 1315, 1300, 1260, 935, 830, 765, 725, 702, 495, 425, *333, 322*
2-Brt	1626, 1539, 1501, 1374, 1315, 1294, 1280, 1154, 1088, 1042, 1035, 885, 804, 772, 737, 620, 500, 487, *335, 324,* 228
213-Btd	1620, 1525, 1310, 1140, 1130, 960, 935, 830, 745, 655, 412, *341, 326,* 233
123-Btd	1630, 1585, 1540, 1450, 1430, 1280, 1230, 1010, 945, 795, 780, 760, 720, 700, 580, 498, 485, 430, *345, 338,* 354, 243
N-Miz	1710, 1620, 1535, 1425, 1285, 1260, 1247, 1110, 1020, 970, 850, 785, 760, 665, 620, 333, *325, 315,* 289, 278, 261
Iz	1610, 1535, 1496, 1423, 1315, 1262, 1176, 1128, 1060, 850, 750, 725, 650, 612, *326, 318*

[a]Values in italics are assigned as the Pt–Cl stretching mode.

For *cis*-$Pt(NH_3)(Tz)Cl_2$ the mode associated with stretching of the C–C and C–N bonds in the thiazole ring is shifted to higher frequencies by 35 ± 10 cm^{-1} on complexation. Appreciable change occurs on complexation for the band appearing at 860 cm^{-1} in the pure ligand. No band at this frequency is found in the spectrum of the complex. This band has been associated with the bending vibration of the N heteroatom and the stretching of the C–S bond. However, the presence of other fundamentals near this region makes the localization of that absorption difficult if shifting occurs.

For *cis*-$Pt(NH_3)(2\text{-Brt})Cl_2$ the mode associated with the stretching of the C=C and C–N bonds shows a shift of 20 ± 10 cm^{-1} to higher frequencies on complexation. The stretching mode involving C=C and C=N does not show appreciable shifting.

The medium-range infrared spectrum of *cis*-$Pt(NH_3)(Bt)Cl_2$ shows smaller changes for absorptions due to ligand vibrations than the systems already discussed. The band occurring at 1590 cm^{-1} in the ligand shows a shift of 20 ± 10 cm^{-1} to higher frequencies. In the region 900–700 cm^{-1} noticeable changes are observed. The strong band at 870 cm^{-1} in the ligand is not present at that frequency in the complex. Also, strong bands at 790 and 660 cm^{-1} do not appear in the spectrum of the complex. Complexation of platinum to benzothiazole in *cis*-$Pt(NH_3)(Bt)Cl_2$ shows a large effect on vibrations of the ligand that can be related to the γN mode and the C–S stretching mode, as well as other related vibrations.

The infrared spectrum of *cis*-$Pt(NH_3)(123\text{-Btd})Cl_2$ shows appreciable changes in ligand vibrations upon complexation. The band corresponding to 1340 cm^{-1} in the ligand disappears in the complex. Also, the strong band at 895 cm^{-1} disappears in the complex and the band at 715 cm^{-1} in the ligand is shifted by 15 cm^{-1}. The spectral changes observed in ligand vibrations are related to nitrogen and sulfur heteroatoms as in the other cases already discussed.

The infrared spectrum of *cis*-$Pt(NH_3)(213\text{-Btd})Cl_2$ also shows appreciable changes for the vibrations of 213-Btd. The band at 810 cm^{-1} in the ligand almost disappears in the complex and a shift of 20 ± 10 cm^{-1} to lower frequencies is observed for the band at 850 cm^{-1}. Also, bands at 980 and 950 cm^{-1} are shifted to 960 and 935 cm^{-1}, respectively.

The infrared spectrum of *cis*-$Pt(NH_3)(N\text{-Miz})Cl_2$ shows absorptions due to ligand vibrations. Most of the absorption bands are shifted by less than 20 cm^{-1} upon complexation. The exception is the ring stretching vibration at 909 cm^{-1} in the spectrum of the free ligand, which appears at about 970 cm^{-1} in the spectrum of the complex. This is characteristic of *N*-methylimidazole coordination [18]. Vibrations that are shifted include both νC–H at 744 and 821 cm^{-1}, and δC–H vibrations appearing at 1078 and 1109 cm^{-1} in the pure ligand [19].

In the infrared spectrum of *cis*-$Pt(NH_3)(Iz)Cl_2$, the band which is shifted the most is that corresponding to the ring stretching vibration, which appears at 936 cm^{-1} in the free ligand [18]. That band appears at 960 cm^{-1} in the complex. Shifts near 20 cm^{-1} to lower frequencies are observed for the region 1142–1541 cm^{-1}.

Tentative assignment of the ν(Pt–Cl) bands is simplified by their high intensities. With the exception of the thiazole complex, all the mixed ligand complexes have two Pt–Cl stretching bands that are separated by more than 10 cm^{-1}. The ν(Pt–Cl) frequencies for the new complexes are in italics in Table III. The far-infrared evidence is conclusive with respect to the *cis* geometry of the complexes.

The ν(Pt–Cl) frequencies observed for complexes containing the thiazole moiety are consistent with nitrogen coordination to the heterocyclic ligands. Also, the small splitting of the bands is not consistent with coordination through the sulfur heteroatom. On the other hand, the far-infrared spectral data for benzothiadiazole complexes fit with sulfur coordination to platinum.

UV–Vis Spectral Data

The UV–Vis spectra were the most useful for assigning the mode of coordination of the heterocyclic ligands. The complexes with Tz, 2-Brt and Bt all had weak absorption bands in the 355–365 nm range, as did the N-Miz and Iz complexes (see Table IV). These are characteristic of *cis*-PtL_2Cl_2 complexes where L is N-coordinated [20]. However, the 213-Bdt and 123-Bdt complexes both had weak bands at 420 nm. This significant shift to longer wavelength agrees with the assignment of coordination through S by these two ligands.

TABLE IV. UV–Vis Absorption Maxima for *cis*-$Pt(NH_3)(L)Cl_2$ in 5% DMSO–H_2O

L	Wavelength (nm) (ϵ)
Tz	360(69), 310(100), 260(1.1×10^3), 240(2.2×10^3)
Bt	365(53), 325(100), 294sh, 270(2.1×10^3), 264(2.3×10^3)
2-Brt	360(97), 305(243), 253(3.1×10^3)
213-Bdt	420sh, 350(3×10^2), 311(8.9×10^2)
123-Bdt	420sh, 310(3.0×10^3)
N-Miz	365sh, 320sh (very dilute in H_2O)
Iz	355sh, 310sh (very dilute in H_2O)

Cytotoxicity Results

Four complexes were sufficiently soluble to permit the determination of growth inhibition under the standard conditions established for screening, using KB cells. All four showed cytotoxic activities. The ED_{50} values (μg/ml) for *cis*-$Pt(NH_3)(L)Cl_2$ were 2.0 for L = Tz, 2.0 for 2-Brt, 0.3 for Bt and 2.0 for 213-Btd.

Conclusions

The mixed ammine–ligand complexes do indeed show cytotoxicity, but low solubilities in water and difficulties in preparation may well preclude further studies on these complexes. The spectral evidence shows that the ligands containing the thiazole ring are all coordinated to the Pt through the N, not, as originally hoped, through the S heteroatom. However, the two complexes containing benzothiadiazoles clearly are coordinated through the S rather than the N atoms.

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