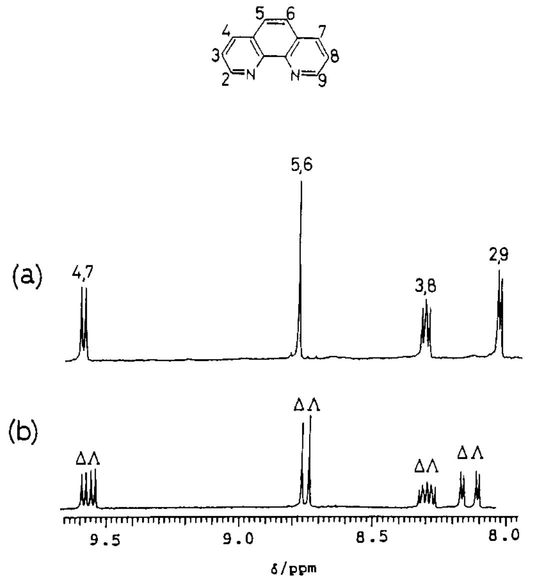

Figure 4. ^{1}H NMR spectra (500 MHz) of $[Si(phen)_3]^{4+}$ (ca. 0.004 M) in D_2O, (a) in the absence and (b) in the presence of $Na_2[Sb_2\{(+)\text{-tart}\}_2]$ (0.08 M).

chemical shift difference between the enantiomers due to the addition of the eluting agent is observed for the 6,6′-protons (0.1 ppm) of $[Si(bpy)_3]^{4+}$ and for the 2,9-protons (0.1 ppm) of $[Si(phen)_3]^{4+}$. This suggests that ((+)-tartrato)antimonate(III) ions are near these protons; that is, they approach along the direction of the C_3 axis of the complex ions. The shifts of the 2,9-proton signals upon the addition of the eluting agent are larger than those of the 6,6′-proton signals. This finding is in accordance with the more effective resolution of $[Si(phen)_3]^{4+}$ as compared to $[Si(bpy)_3]^{4+}$. The symbols Δ and Λ in Figure 4b indicate that the signals are attributable to Δ- and Λ-$[Si(phen)_3]^{4+}$, respectively. The assignments are based on the measurements for the individual enantiomers in the presence of the eluting agent. Upon the addition of $Na_2[Sb_2\{(+)\text{-tart}\}_2]$, the 2,9-proton signals of the Δ isomer shift to the lower magnetic field side more than those of the Λ one. It appears that the eluent anion interacts more strongly with the Δ cation than with the Λ one. If only a 1:1 ionic interaction is taken into account, it is difficult to explain the chromatographic elution order, for an isomer with a stronger interaction with the eluting agent usually has a larger elution rate.

In general, the chromatographic elution of ionic species largely depends on the degree of electric neutralization, such as the formation of ion pairs. In the present case, it is considered that the formation of the higher ion pairs may play a dominant role in the electric neutralization. In future work, we will carry out ion association measurements and elucidate the chromatographic elution mechanism.

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Articles

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Complexes of Platinum(II) with the Polymeric Amine Ligand Polyaziridine

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$K_2[PtCl_4]$, *cis*-$Pt(NH_3)_2Cl_2$, $Pt(en)Cl_2$, and $Pt(bpy)Cl_2$ form complexes in aqueous solution with polyaziridine, the polymeric amine ligand $\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}$ (PEI), as investigated by UV/Vis and ^{195}Pt NMR spectroscopy. The interaction of $K_2[PtCl_4]$ and $Pt(bpy)Cl_2$ with PEI yields unambiguously "single species" $Pt(PEI)_4{}^{2+}$ and $Pt(bpy)(PEI)_2{}^{2+}$, respectively. For *cis*-$Pt(NH_3)_2Cl_2$ and $Pt(en)Cl_2$, interaction with PEI leads to release of ammonia and ethylenediamine, as detected by ^{14}N NMR spectroscopy. Several products are obtained in these cases. The kinetics of the formation of $Pt(PEI)_4{}^{2+}$ follows a rate law $r = k_{obs}[PtCl_4{}^{2-}]$, where k_{obs} increases with increasing PEI concentration and decreases with decreasing pH. Pt(II)–PEI complexes containing "free" amine donor groups form mixed Pt(II)–Cu(II) complexes, in which the magnetic interactions are altered, as compared with the Cu(II)–PEI complexes.

Introduction

Complexes of platinum(II) were instrumental for the establishment of the coordination theory;[1] they played an important role in the development of coordination chemistry ever since,[2] and they found an unexpected and important application as anticancer agents.[3]

Much effort has been devoted to elucidate the mechanism of the cytotoxic reactions in the latter application.[4] It has been found that the *cis*-$Pt(NH_3)_2Cl_2$ complex interacts with the biomacromolecule DNA, in a way which blocks the further reproduction of the cells. Many details of this mechanism are known today, which makes the design of new drugs possible.

In our systematic investigation of complex formation with synthetic polymeric amine ligands,[5] we studied the interaction of various platinum(II) complexes with branched poly(ethyleneimine) (polyaziridine) (I) with two aims: (i) to establish the mechanisms of the interaction of simple platinum ccmplexes with a simple polymer and (ii) to modify the properties of the latter through this complexation.

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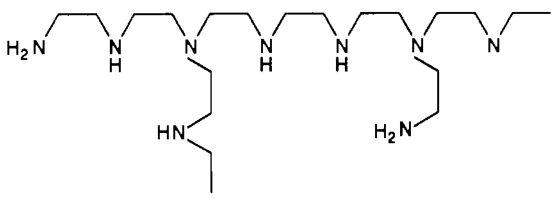

polyethyleneimine (I) = polyaziridine (PEI)

The complex formation of polyaziridine with platinum(II) has been reported in the literature before.[6] In these investigations, however, only "stoichiometric" interactions were considered, which give invariably insoluble products, probably through cross-linking of the polymers. We have confined our investigations to aqueous solutions, which stay homogeneous through complexation. The platinum complexes used were $PtCl_4^{2-}$ or $Pt(LL)Cl_2$ [where LL = *cis*-$(NH_3)_2$, ethylenediamine, and 2,2-bipyridine].

Experimental Section

Materials. The starting materials $K_2[PtCl_4]$, *cis*-$Pt(NH_3)_2Cl_2$, Pt(en)Cl_2, and Pt(bpy)Cl_2 were prepared by literature procedures.[7-10] [Pt(en)$_2$]Cl_2 and [Pt(bpy)en]$(PF_6)_2$, synthesized for comparison purposes, were prepared according to standard methods.[9,11] The ligands ethylenediamine and 2,2′-bipyridine were purchased from Fluka and were used without further purification. Branched poly(ethyleneimine) (PEI, designated as polyaziridine in Chemical Abstracts) was obtained from Fluka (Polyimin P) as 50% aqueous solution. It has a mean molecular weight in the range of ca. 6.0×10^5 to 1.0×10^6 g mol^{-1}. PEI is a polyamine ligand comprising primary, secondary, and tertiary amine groups in a ratio of ca. 1:2:1. That means it is a highly branched polymer. Every chelating unit, however, is similar to ethylenediamine. The concentration of the ligating units is expressed by the number of moles of nitrogen (monomer unit, $-CH_2-CH_2-NH-$, PEI, used as abbreviation of one N-containing unity in formulas) per liter of solution.

Physical Measurements. Electronic spectra were taken on a Perkin-Elmer 555 UV/vis spectrophotometer. ^{195}Pt and ^{14}N NMR spectra were run on a Bruker AM-360-MHz instrument in aqueous solution, using 10-mm diameter tubes. Solutions 10^{-1}–10^{-2} M in platinum with ca. 10% of D_2O were employed. ^{195}Pt NMR chemical shifts are reported relative to an aqueous solution of K_2PtCl_6. ^{14}N chemical shifts are given relative to nitromethane, contained in a coaxial capillary. Comparison was also made, using tetraethylammonium chloride as an internal reference. All ^{195}Pt and ^{14}N NMR spectra were obtained from overnight accumulations. EPR spectra at room temperature and in frozen solution were recorded on a Bruker ESP 300 spectrometer operating at 9.7 GHz. Spectra at low temperature were taken in a liquid nitrogen Dewar inserted in the EPR cavity. Calibration of *g* values was based on 2,2-diphenyl-1-picrylhydrazyl (DPPH) (g = 2.0036).

Preparation of Complexes. $Pt(PEI)_4^{2+}$. The complex formation occurs by ligand exchange reaction with $PtCl_4^{2-}$, in aqueous solution at room temperature. $K_2[PtCl_4]$ was added to partially protonated PEI in various stoichiometric amounts according to

$$PtCl_4^{2-} + nPEI + xH^+ \rightarrow Pt(PEI)_4^{2+} + (n-4)PEI + xH^+ + 4Cl^- \quad (1)$$

where n = 6 (x = 0.75); 8 (1.00); 12 (1.50); 16 (2.00). The best pH range for the preparation of complexes is 6–8. The reaction was followed by UV/Vis spectroscopy in the range 200–600 nm, where $PtCl_4^{2-}$ is the only absorbing species.

Reactions of *cis*-$Pt(NH_3)_2Cl_2$ and Pt(en)Cl_2 with PEI. A suspension of each platinum complex (0.20 mmol) in water, containing partially protonated PEI [3.2 mmol of PEI and 0.40 mmol of H^+ (HCl); 1 Pt^{2+}:16 PEI:2 H^+] was refluxed for 30 min at 60 °C.

Pt(bpy)$(PEI)_2^{2+}$. PEI was added (32 mmol) to a suspension of Pt(bpy)Cl_2 (0.844 g, 2.0 mmol; 1 Pt^{2+}:16 PEI) in water. By refluxing for 3 h at 80 °C, a homogeneous yellow solution was obtained. The reaction was also performed for a concentration ratio 1 Pt^{2+}:8 PEI.

Table I. Position and Extinction Coefficients of Absorption Bands of Pt(II)–Polyaziridine Complexes in Aqueous Solution

complexes	λ_{max}/nm (ϵ/M^{-1} cm^{-1})
$Pt(PEI)_4^{2+}$	280 sh[a] (128)
cis-DDP[b] + 16 PEI + 2 H^+	280 sh (50); 210 (3000)
Pt(en)Cl_2 + 16 PEI + 2 H^+	280 sh (50); 210 (3000)
Pt(bpy)(en)$^{2+}$	445 sh (4.4); 415 sh (13); 316 (17 182); 305 (11 954); 242 (20 545)
Pt(bpy)$(PEI)_2^{2+}$	318 (10 269); 307 (7923); 296 (5577); 284 (5617); 240 (15 597)

[a] sh, shoulder. [b] *cis*-DDP, *cis*-$Pt(NH_3)_2Cl_2$.

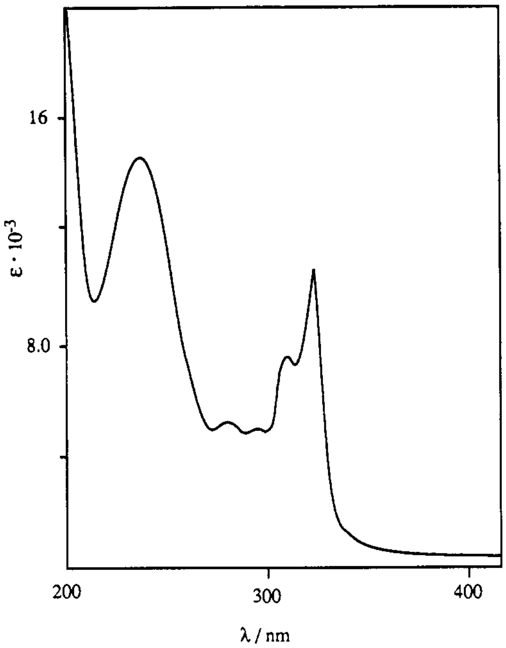

Figure 1. Absorption spectrum of Pt(bpy)$(PEI)_2^{2+}$ in aqueous solution.

Solution Studies. Potentiometric Titrations. The concentration of PEI was kept constant 8.0×10^{-3} M, HNO_3 was added in excess (1.6×10^{-2} M) and back titrated with NaOH 0.1 M. The ionic strength was adjusted to 0.5 M with KNO_3. Samples of $Pt(PEI)_4^{2+}$ were prepared 24 h in advance, by adding $K_2[PtCl_4]$ to protonated PEI. For Pt(bpy)$(PEI)_2^{2+}$ samples, the acid was added after complex formation. The titrations were performed on a Mettler DL 21 automatic titrator, and the pH was measured with a glass electrode.

EPR Spectroscopy. Cu^{2+}(aq) was added in various stoichiometric amounts to solutions of partially protonated PEI, $Pt(PEI)_4^{2+}$, and Pt(bpy)$(PEI)_2^{2+}$. These solutions had concentration ratios of 16 PEI:2 H^+ and 8 PEI:1 H^+, except for Pt(bpy)$(PEI)_2^{2+}$ complex solutions, to which no acid was added. The ratio PEI:Pt^{2+} was 16 and 8, respectively. The concentration of Pt(II) was kept constant at 1.0×10^{-2} M, and Cu^{2+} was varied from 1.0×10^{-3} M up to values corresponding to "overloading" of PEI, assuming the presence of $Pt(PEI)_4^{2+}$ or Pt(bpy)$(PEI)_2^{2+}$ and $Cu(PEI)_4^{2+}$ complexes.

Results and Discussion

UV/Vis Spectra and Species Formed. The spectra of solutions obtained upon reaction between $PtCl_4^{2-}$ and PEI, for ratios 6 ≤ PEI:Pt^{2+} ≤ 16, exhibit no absorption bands above 250 nm, except a shoulder of low intensity at 280 nm (Table I). The disappearance of the bands at 390 and 328 nm present in the spectrum of $PtCl_4^{2-}$ due to ligand field transitions clearly indicates that platinum was complexed by PEI. Furthermore the spectra of those solutions closely resemble those of $Pt(NH_3)_4^{2+}$ and Pt(en)$_2^{2+}$.[12-14] The shoulder at 280 nm (ϵ = 128 M^{-1} cm^{-1}) is assigned to a spin forbidden d–d transition according to the attribution of Mason

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et al.[12,13] in the spectrum of $Pt(NH_3)_4^{2+}$. The formation of a PtN_2Cl_2 chromophore is ruled out by the absence of bands in the visible region.[14] It seems clear, therefore, that $Pt(PEI)_4^{2+}$ is the "single species" present in solution.

The spectra of both *cis*-$Pt(NH_3)_2Cl_2$ and $Pt(en)Cl_2$, after reaction with PEI, present an intense absorption band at 210 nm and a weak shoulder at 280 nm (Table I). On the basis of its high intensity, the band at 210 nm arises probably from a dipole allowed d–p transition by analogy with the spectrum of $Pt(NH_3)_4^{2+}$ that presents a band at 198 nm assigned to a d–p transition with similar intensity ($\epsilon \approx 10^3$).[12-14] The shoulder at 280 nm corresponds to a spin forbidden d–d transition, according to the assignment made for $Pt(NH_3)_4^{2+}$ by Mason.[12] For both cases, the identification of the chromophores of the species obtained upon reaction with PEI cannot be indicated on the basis of the UV/Vis spectroscopy alone (vide infra, ^{195}Pt NMR) because it does not provide sufficiently distinct spectral features to identify the species. Indeed, other species besides $Pt(NH_3)_2(PEI)_2^{2+}$ and $Pt(en)(PEI)_2^{2+}$, namely $Pt(PEI)_4^{2+}$, cannot be ruled out by the absorption spectra.

The interaction of $Pt(bpy)Cl_2$ with PEI, for PEI:Pt^{2+} = 8 and 16, leads to pale yellow solutions, whose spectra show a quite intense absorption in the 220–380-nm region (Figure 1). These spectra are very similar to the ones of $Pt(bpy)(en)^{2+}$ and $Pt(bpy)(NH_3)_2^{2+}$.[15,16] The strong absorption bands centered at ~240 nm and two slightly weaker ones at ~307 and ~318 nm are present in both spectra of $Pt(bpy)(en)^{2+}$ and $Pt(bpy)(PEI)_2^{2+}$. There are subtle differences, however: The "fine structure" situated in the long wavelength part of the spectrum of $Pt(bpy)(en)^{2+}$ at ca. 445 and 415 nm, respectively, is no longer discernible in the spectra of $Pt(bpy)(PEI)_2^{2+}$, and two new weak lines at 284 and 296 nm appear in the spectra of the latter. These observations strongly indicate the formation of $Pt(bpy)(PEI)_2^{2+}$. For this type of Pt(II) α-diimine complexes containing in addition a strong field ligand (e.g., en, PEI), the ligand field transitions are predicted to occur below 350 nm. However, the ligand field absorption features are not observed because they are obscured by intense intraligand (π–π^*) and MLCT absorption bands.[17] The bands at 307 and 318 nm are assigned to bipyridine centered π–π^* transitions.[15,16] The intense absorption band at 240 nm is attributed to a MLCT transition, according to the assignment of Gillard et al.[18] in the spectrum of $Pt(bpy)Cl_2$ on the basis of solvent sensitivity. This band is not present in the spectrum of $Zn(bpy)_3^{2+}$; and since this complex has *no* MC or MLCT transitions, the possibility that it arises from a LC transition is excluded.[15] Therefore, the presence of this band in the spectrum rules out the displacement of bipyridine by PEI and confirms the formation of $Pt(bpy)(PEI)_2^{2+}$.

^{195}Pt and ^{14}N NMR. The interaction of the various platinum complexes with PEI was investigated by ^{195}Pt NMR spectroscopy. This technique has been extensively used in the study of platinum(II) complex reactions in aqueous solution, since the discovery of antitumor properties of *cis*-$Pt(NH_3)_2Cl_2$. Indeed, ^{195}Pt NMR spectroscopy is a very powerful tool in platinum solution chemistry owing to (i) the large chemical shift range (~15 000 ppm), being sensitive to subtle changes in molecular environment[19-22] and (ii) ligand exchange reactions of Pt(II) are usually slow enough on the NMR time scale to allow the observation of separate resonances for each distinct platinum complex in solution.[23,24]

Table II. ^{195}Pt NMR Chemical Shift Data[a] of Various Pt(II) Complexes with Polyaziridine

complexes	chemical shift/ppm
$Pt(en)_2^{2+}$	−2999
$Pt(PEI)_4^{2+}$ [1 Pt^{2+}:16PEI:2 H^+(HCl)]	−2958
$Pt(PEI)_4^{2+}$ [1 Pt^{2+}:16PEI:2 H^+(HNO_3)]	−2958, −2879
$Pt(PEI)_4^{2+}$ [1 Pt^{2+}:8PEI:2 H^+(HNO_3)]	−2956, −2882
cis-DDP[b] + 16 PEI + 2 H^+(HCl)	−2885, −2748, −2111, −1786
$Pt(en)Cl_2$ + 16 PEI + 2 H^+(HCl)	−2975, −2894, −2042, −1784
$Pt(bpy)(en)^{2+}$	−2812
$Pt(bpy)(PEI)_2^{2+}$ (1 Pt^{2+}:16 PEI)	−2782
$Pt(bpy)(PEI)_2^{2+}$ (1 Pt^{2+}:8 PEI)	−2778

[a] ^{195}Pt NMR chemical shifts, measured in aqueous solution at 360 MHz, were referenced to $K_2[PtCl_6]$. [b] *cis*-DDP, *cis*-$Pt(NH_3)_2Cl_2$.

The ^{195}Pt chemical shift data obtained upon interaction of the various platinum complexes with PEI are summarized in Table II.

^{195}Pt NMR spectra of solutions, which contain according to UV/Vis spectra the $Pt(PEI)_4^{2+}$ complex, consist of only one line at −2958 ppm relative to $K_2[PtCl_6]$, if HCl is used as acid. This strongly indicates a "single species" $Pt(PEI)_4^{2+}$, in agreement with the results from UV/Vis spectroscopy. Indeed, the chemical shift of this signal is close to that observed for $Pt(en)_2^{2+}$ (Table II). The formation of species with the general formula $PtN_{3-x}Cl_x$ (x = 0, 1, 2) and $PtN_{3-y}O_y$ (y = 0, 1, 2), upon interaction of $PtCl_4^{2-}$ with PEI, is once again excluded since their resonance lines appear downfield relative to PtN_4 chromophores in the window ranges of (−2421, −2121 ppm) and (−2121, −1571 ppm), respectively.[24] If HNO_3 is used as an acid (at the same concentration, as HCl), a second signal appears at ca. −2881 ppm, which is still well within the chemical shift range observed for PtN_4 species (Table II). These two signals can be due to "species", which are slightly different either in their first or second sphere configurations.

The ^{195}Pt NMR spectrum of *cis*-$Pt(NH_3)_2Cl_2$ after interaction with PEI, at pH 9, exhibits four resonance lines (Table II). This observation clearly shows that PEI induced release of ammonia, with the consequent formation of a variety of "species". An interpretation of these signals can be given, comparing the chemical shift values with data reported in the literature for Pt(II)–amine complexes.[21,23-32] The peaks, present in the spectrum of *cis*-$Pt(NH_3)_2Cl_2$ upon interaction with PEI, at −2885 and −2748 ppm (highest intensity) are well within the range of PtN_4 chromophores. They therefore correspond to the formation of $Pt(PEI)_4^{2+}$ and $Pt(NH_3)_2(PEI)_2^{2+}$, respectively. The two peaks present in the downfield region at −2111 and −1786 ppm are due to the displacement of ammonia, which is substituted by OH^- or H_2O in a first step.[21,25,28-32] They probably correspond to species containing one and two oxygen donor atoms in the coordination sphere, respectively. In general, the more electronegative oxygen donor (O_d) produces a chemical shift that is downfield relative to a nitrogen donor (N_d), and therefore the chemical shifts of the complexes *cis*-$Pt(NH_3)_2L_2$ are found to increase in the order *cis*-$Pt(NH_3)_2(N_d)_2$ < *cis*-$Pt(NH_3)_2(N_d)(O_d)$ < *cis*-$Pt(NH_3)_2(O_d)_2$.[26]

However, the identification of the species formed is not certain on the basis of ^{195}Pt NMR spectroscopy alone. Indeed, kinetic studies concerning the hydrolysis of *cis*-$Pt(NH_3)_2Cl_2$ in aqueous solution revealed that the monomer, dimer, and trimer (hydroxide-bridged) oligomeric species are already formed at neutral

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pH.[23,25,31] The presence of species having Pt–Cl bonds is not very likely, because the hydrolysis of *cis*-$Pt(NH_3)_2Cl_2$ is known to occur through the formation of $Pt(NH_3)_2(H_2O)_2^{2+}$ or $Pt(NH_3)_2(HO)_2$, depending on the pH.[3]

The binding of $Pt(en)Cl_2$ to PEI produced a solution whose spectrum consists of four peaks (Table II). The strongest peak at −2975 ppm is assigned to $Pt(en)(PEI)_2^{2+}$. The other signals, of much lower intensity, present in the downfield region arise because of the release of ethylenediamine. The peak at −2894 ppm is probably due to the formation of $Pt(PEI)_4^{2+}$, although in small amount. The peaks at −2042 and −1784 ppm are assigned to species containing one and two oxygen donor atoms,[27] by similarity with the assignments made for the spectrum of *cis*-$Pt(NH_3)_2Cl_2$ after reaction with PEI. The greater difficulty of PEI in displacing ethylenediamine relatively to ammonia is reflected in the lower intensity of the peaks present in the downfield region (−2120, −1780 ppm). This is quite reasonable because ethylenediamine is a chelating ligand.

After two weeks of reaction with PEI the spectra of the solutions of *cis*-$Pt(NH_3)_2Cl_2$ and $Pt(en)Cl_2$ do not show any peaks in the downfield region (i.e., between −2120 and −1780 ppm). This observation supports our interpretation and shows that loss of ammonia and ethylenediamine is a slow process. Furthermore, it clearly indicates that the displacement of those ligands should proceed through the formation of intermediate species containing oxygen donor atoms, which are later on replaced by the amine groups of the polymer.

Further proof of loss of ammonia and ethylenediamine was furnished by ^{14}N NMR spectroscopy. The line widths of ^{14}N signals are very different, if the nuclei are located either in a polymer species or in small molecules, due to quadrupolar relaxation. The signal of ^{14}N in PEI and in its metal complexes is broadened beyond detection. The formation of NH_4^+ (360 ppm, relative to nitromethane) and enH_2^{2+} (351 ppm) in the solutions of *cis*-$Pt(NH_3)_2Cl_2$ and $Pt(en)Cl_2$ upon reaction with PEI, at pH 6, can therefore be detected conveniently by the appearance of the corresponding relatively narrow ^{14}N signals.

The ^{195}Pt NMR spectra of solutions of $Pt(bpy)Cl_2$, after reaction with PEI, present only one line at ca. −2780 ppm. This value is close to the one observed for $Pt(bpy)(en)^{2+}$ (Table II). Furthermore, the UV/Vis spectra of those solutions are almost identical to the one of $Pt(bpy)(en)^{2+}$.[15] These observations clearly point out the formation of $Pt(bpy)(PEI)_2^{2+}$. The absence of other lines, namely, between −2958 and −2882 ppm [chemical shift range of $Pt(PEI)_4^{2+}$], shows that only one species is formed.

Thus, PEI has the ability to induce release of ligands such as ammonia and ethylenediamine, while the strong chelating bipyridine remains coordinated to platinum upon interaction of $Pt(bpy)Cl_2$ with the polymer. Similar findings are reported in the literature for the interaction of *cis*-$Pt(NH_3)_2Cl_2$, $Pt(en)Cl_2$, and $Pt(bpy)Cl_2$ with amino acids,[30] peptides, and proteins[23] containing a thiol group, at pH 6.

The ^{195}Pt NMR line widths of the resonance lines of Pt(II)–PEI complexes are broader compared to analogous low molecular complexes since the contribution from the chemical shift anisotropy to the relaxation of the platinum nucleus is particularly important in macromolecular complexes because the platinum nucleus has a slower tumbling rate (i.e., a higher rotational correlation time).[5,23,33]

Kinetics of Formation of $Pt(PEI)_4^{2+}$. The reactions were carried out at constant pH (5,6,7,8) at 25 °C, in solutions with $6 \le PEI{:}Pt^{2+} \le 16$. The pH was kept constant by pH-stat method. The concentrations of the reactants were $PtCl_4^{2-}$, 4.98×10^{-3} M, and PEI varied from 2.98×10^{-2} to 7.98×10^{-2} M. The progress of the reaction was followed by scanning the absorption spectrum of the reacting mixture at suitable time intervals in the 600–300-nm region, where $PtCl_4^{2-}$ is the only absorbing species ($\lambda_{max} = 390$ nm; $\epsilon = 55.8\ M^{-1}\ cm^{-1}$). The measurements corresponding to $t = \infty$ were done after 24 h. The spectral sequences yield one isosbestic point at 320 nm for all concentration ratios.

Table III. Observed Pseudo-First-Order Rate Constants[a] ($10^4 k_{obs}/s^{-1}$, $T = 25$ °C) for the Formation of $Pt(PEI)_4^{2+}$ in Aqueous Solutions

	solutions[c]			
pH[b]	1 Pt^{2+}:6 PEI	1 Pt^{2+}:8 PEI	1 Pt^{2+}:12 PEI	1 Pt^{2+}:16 PEI
5	2.19	2.40	2.55	2.62
6	2.33	2.57	2.81	3.00
7	3.64	3.80	4.20	4.40
8	4.32	4.63	5.07	5.39

[a] Observed pseudo-first-order rate constants for the disappearance of $PtCl_4^{2-}$ obtained from eq 2. [b] The pH was kept constant by pH-stat method. [c] $[PtCl_4^{2-}] = 4.98 \times 10^{-3}$ M.

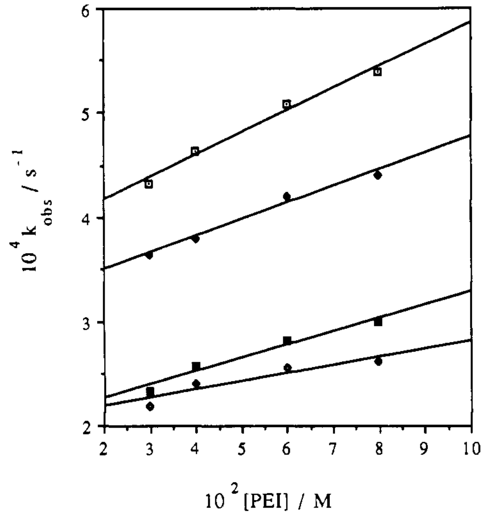

Figure 2. k_{obs} as a function of the total concentration of PEI at four different pH values (◇, pH 5; ◘, pH 6; ◆, pH 7; ⊡, pH 8).

Pseudo-first-order rate constants were determined in general for $t \le 3600$ s. After this time the plots $\ln\{(A_\infty - A_0)/(A_\infty - A_t)\}$ vs time deviate from linearity, owing to the very low concentration of $PtCl_4^{2-}$. Pseudo-first-order rate constants k_{obs} were calculated from the integrated first-order equation

$$\ln\{(A_\infty - A_0)/(A_\infty - A_t)\} = k_{obs}\, t \qquad (2)$$

The data reported in Table III show that the rate of the reaction increases with the concentration of PEI and with increasing pH. The observed rate constants are nearly a linear function of pH in the range $5 \le pH \le 8$, which is due to the almost linear dependence of the concentration of unprotonated PEI on pH in this range. At a given pH, plots of k_{obs} against [PEI] are linear (Figure 2). Hence, the experimental results at constant pH are consistent with a rate law expressed by

$$-d[PtCl_4^{2-}]/dt = k_{obs}[PtCl_4^{2-}] \qquad (3)$$

This rate law corresponds to the expression that is typical for square-planar substitution reactions of Pt(II).[34,35] In fact, the observed pseudo-first-order rate constants agree fairly well with the values reported in the literature for monodentate[36] and polydentate amines.[37–39] In substitution reactions of square-planar Pt(II) complexes with polydentate amine ligands, the rate-determining step is usually the substitution of the first leaving group, whereas the fast bimolecular step corresponds to the ring closure.[34,35] Thus, it is reasonable to postulate that the first step in

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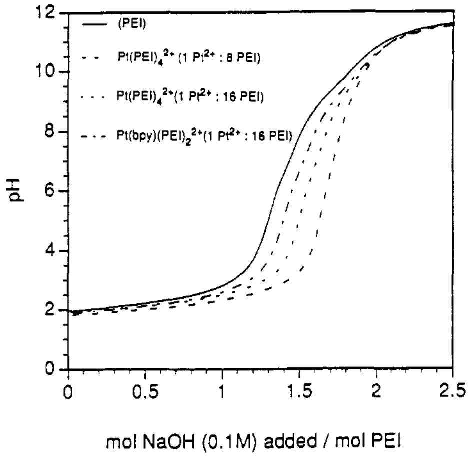

Figure 3. Titration curves with NaOH (0.1 M) of PEI, PEI loaded with $Pt(PEI)_4^{2+}$, and $Pt(bpy)(PEI)_2^{2+}$. [PEI] = 8.0×10^{-3} M; $[H^+]_i = 1.6 \times 10^{-2}$ M.

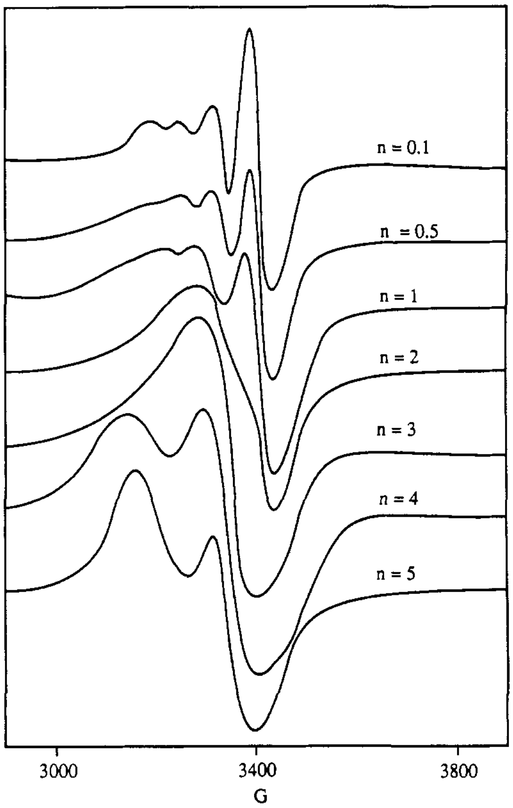

Figure 4. EPR spectra in aqueous solution of Cu(II)–PEI complexes at room temperature for solutions having 16 PEI:2 H^+:*n* Cu^{2+}.

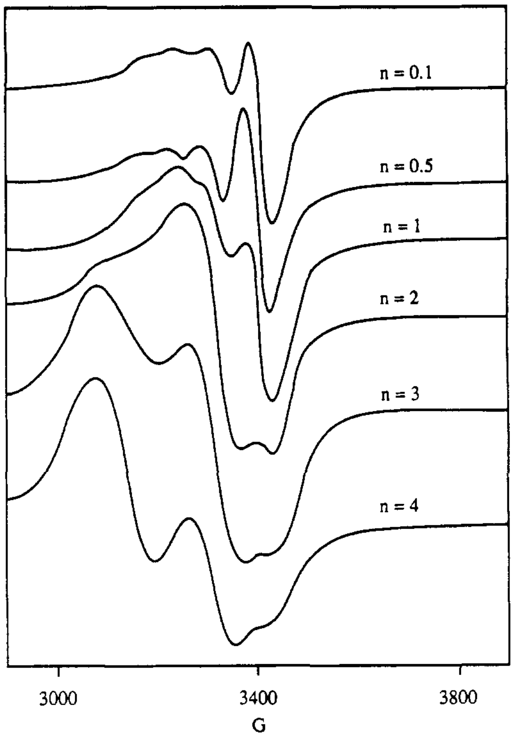

Figure 5. EPR spectra in aqueous solution of mixed Cu(II)/Pt(II) PEI complexes at room temperature for solutions having 1 Pt^{2+}:16 PEI:2 H^+:*n* Cu^{2+}.

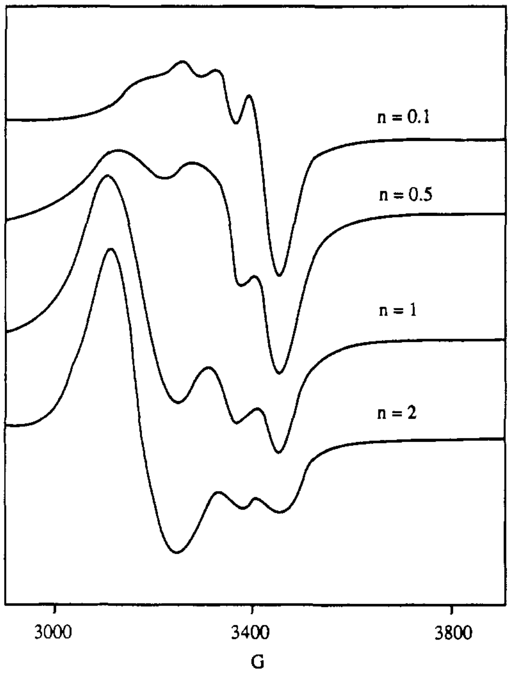

Figure 6. EPR spectra in aqueous solution of mixed Cu(II)/Pt(II) PEI complexes at room temperature for solutions having 1 Pt^{2+}:8 PEI:1 H^+:*n* Cu^{2+}.

the formation of $Pt(PEI)_4^{2+}$ complex is the slow first-order hydrolysis of $PtCl_4^{2-}$ followed by the replacement of H_2O (in the hydrolyzed species) by an unprotonated amine group of the polymer and ring closure with the formation of the other Pt–N bonds.

Potentiometric Titrations. PEI is a strong polybase which behaves markedly different compared to the corresponding monomers owing to the three different kinds of amine groups, its branched structure, and the nearest neighbor interactions (formation of hydrogen bonds and electrostatic repulsion).[40]

Titration curves of solutions of Pt(II)–PEI complexes are displaced to lower pH as compared to that of PEI itself (Figure 3). Moreover, the acidity increases with the concentration of platinum. This shows that platinum is coordinated to PEI, and it occupies nitrogen sites which are no longer available for protonation. The titration curve of solution of the $Pt(bpy)(PEI)_2^{2+}$ complex is shifted to higher pH compared to that of $Pt(PEI)_4^{2+}$ (with the same PEI:Pt^{2+} ratio), indicating that in the first case platinum is bound to a lower number of nitrogen atoms of the polymer.

EPR Spectroscopy. The goal of our study is to obtain information on the local environment of Cu^{2+} as a function of its concentration and of the number of "free" nitrogens available for coordination. In this way, information about the distribution and the interaction between the Cu^{2+} ions can be obtained.

Cu^{2+} complexes with PEI, which does not contain any other metal ion have been studied in detail before.[5] Solutions containing

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[40] Horn, D. In *Polymeric Amines and Ammonium Salts*; Goethals, E. J., Ed.; Pergamon Press: New York, 1980, p 333.

a high ratio of PEI:Cu^{2+} (>20) show EPR spectra of $Cu(PEI)_4{}^{2+}$ or $Cu(PEI)_5{}^{2+}$ complexes (depending on the pH value) in which the anisotropic features are very prominent due to the slow tumbling rate of the macromolecules. This kind of spectra exhibiting copper hyperfine structure is a direct confirmation of the binding of Cu^{2+} to the polymer. Solutions containing PEI, which is more loaded with Cu^{2+} (PEI:Cu^{2+} < 10), yield isotropic broaden line spectra due to the exchange interaction between the paramagnetic centers (Figure 4, $n = 2, 3$), even if the total concentration of Cu^{2+} is low. Indeed, with increasing Cu^{2+} concentration the number of "free" nitrogen sites available for coordination diminishes, and Cu^{2+} ions are constrained to occupy neighboring positions in the polymer coil. The phenomenon of exchange Cu^{2+}–Cu^{2+} interactions has been called the "clothes-line" effect.[5] A further decrease of the PEI:Cu^{2+} ratio (≤5) yields spectra in which the signals of Cu^{2+}(aq) and of Cu^{2+} bound to PEI are clearly discernible (Figure 4, $n = 4, 5$). The appearance of the signal corresponding to the formation of Cu^{2+}(aq) species shows that the polymer is completely loaded with Cu^{2+} ions, and consequently no more "free" nitrogen sites are available for coordination.

Figure 5 shows an analogous series of spectra of PEI loaded partially with Pt^{2+} (PEI:Pt^{2+} = 16). As expected, the "clothes-line" effect is enhanced at comparable concentration ratios as compared to "free" PEI. Exchange interactions are already clearly observed in a solution containing PEI:Pt^{2+}:Cu^{2+} = 16:1:1 (Figure 5, $n = 1$), and the relative concentration of the Cu^{2+}(aq) is larger in the solution containing 16 PEI:1 Pt^{2+}:4 Cu^{2+} (Figure 5, $n = 4$), as compared to 16 PEI:4 Cu^{2+} (Figure 4, $n = 4$), indicating a significantly reduced capacity for Cu^{2+} binding of the Pt(II)-loaded PEI. These effects are strongly enhanced in a solution containing PEI:Pt^{2+} = 8 (Figure 6). Cu^{2+}(aq) is already clearly present in a solution containing PEI:Pt^{2+}:Cu^{2+} = 8:1:0.5.

The spectra of solutions containing the $Pt(bpy)(PEI)_2{}^{2+}$ (PEI:Pt^{2+} = 16, 8) show a similar evolution with the increase of Cu^{2+} concentration, as the ones of $Pt(PEI)_4{}^{2+}$.

Spectra in frozen solution are anisotropic only for low Cu^{2+} concentrations, with $g_1 = 2.21$, $g_2 = 2.09$, and $A = 74 \times 10^{-4}$ cm^{-1}; while they become isotropic ($g_{iso} = 2.10$) in solutions with a high content of Cu^{2+}. The line widths in the isotropic spectra were measured from peak to peak. It was found that they narrow with the concentration of Cu^{2+} until saturation of the polymer, and then there is a line broadening for solutions which have "overloaded" PEI. The diminution in the line widths is probably due to the "exchange narrowing" effect observed in concentrated solutions.[41]

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Registry No. $K_2[PtCl_4]$, 10025-99-7; *cis*-$Pt(NH_3)_2Cl_2$, 15663-27-1; $Pt(en)Cl_2$, 14096-51-6; $Pt(bpy)Cl_2$, 13965-31-6.

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Electrochemistry of Rhodium and Cobalt Corroles. Characterization of $(OMC)Rh(PPh_3)$ and $(OMC)Co(PPh_3)$ Where OMC is the Trianion of 2,3,7,8,12,13,17,18-Octamethylcorrole

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The first oxidative electrochemistry of rhodium(III) and cobalt(III) corroles is reported in tetrahydrofuran, *N*,*N*-dimethylformamide, benzonitrile, and dichloromethane containing tetrabutylammonium perchlorate as supporting electrolyte. The investigated compounds are represented as $(OMC)Rh(PPh_3)$ and $(OMC)Co(PPh_3)$ where OMC is the trianion of 2,3,7,8,12,13,17,18-octamethylcorrole. Each complex undergoes up to three oxidations and two reductions depending upon solvent. The oxidations occur at the corrole π-ring system while the reductions occur at the rhodium or cobalt metal center. The three one-electron oxidations are electrochemically reversible by cyclic voltammetry at fast potential scan rates, but several chemical reactions occur at lower scan rates or in the presence of added triphenylphosphine. An overall oxidation reduction mechanism is proposed for each complex and comparisons are made with the well-characterized reactions of cobalt and rhodium tetraphenylporphyrins under the same experimental conditions.

Introduction

The electrochemistry of numerous metalloporphyrins has been reported under various solution conditions.[1] Complexes with 55 different elements have been characterized, and the use of these compounds in a variety of applications is well documented in the literature.[2,3] A number of porphyrin-like derivatives have also been studied. One such set of compounds are the corroles, which have a highly conjugated π electron system[4–7] but differ from the porphyrins in that they have a direct linkage between two pyrrole rings of the macrocycle. This structural difference gives rise to a deformation of the ligand so that none of the pyrrole rings can be completely in the same plane of the macrocycle.[8,9] Despite the fact that the corrole cavity is much smaller than that of porphyrins, the system is rather flexible and can accommodate large metal ions without substantial distortion of the macrocycle plane.[9] In the case of cobalt corroles, for which a crystal structure has been reported, the average Co–N distance is 1.87 Å.[10] This is analogous to the corresponding distance in cobalt complexes

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