Articles

Distribution of Halogen Atoms in Mixed-Valence Linear-Chain Complexes of Platinum: A Solid-State ^{15}N NMR Study

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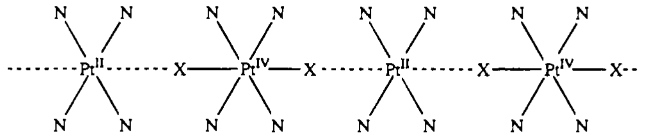
High-resolution solid-state ^{15}N NMR spectroscopy is used to demonstrate unambiguously the presence of Cl−Pt^{IV}−Br units in $[\mathrm{Pt(en)_2}][\mathrm{Pt(en)_2Cl_{2-2x}Br_{2x}}](\mathrm{ClO_4})_4$ complexes ($0 \le x \le 1$). The spectra provide information on the distribution of the halogen atoms around the Pt(IV) sites and allow a measure of the bromine concentration in the chain to be made. It is demonstrated that the halogen distribution is fairly close, but not identical, to random about this site. This suggests that the overall distribution of halogen atoms throughout the mixed-valence chain can be treated as being virtually random.

Introduction

Mixed-valence linear-chain complexes of platinum have been of interest for some time due to their highly anisotropic optical and conductivity properties.[1−5] They also provide good models on which to test theoretical predictions of the behavior of quasi-one-dimensional materials. The structure of these chains consists of a short Pt^{IV}−X distance and a long Pt^{II}−X one (X = Cl, Br, or I) and so can be considered to be a Peierls-distorted version of a symmetric chain; in general, amines occupy the equatorial positions.



One crucial aspect of the complexes is the oxidation states of the metal atoms, and it has been suggested that there may be significant valence delocalization along the chain. It has also been pointed out that a small number of defect species present in the chain, such as Pt(III) sites,[6,7] would have a similar influence to those of polarons and/or solitons in other one-dimensional conductors such as *trans*-polyacetylene,[8,9] and there have been several papers predicting the effects of such defects on the properties of these materials.[10−12]

Recently, solid-state NMR spectroscopy has been used as an indirect probe of metal oxidation state in an attempt to shed more light on the unusual properties of these complexes.[13−15] Studies using ^{195}Pt NMR are handicapped by the large chemical shift anisotropies of the Pt(II) sites which makes spectral acquisition fairly demanding.[14] On the other hand, ^{15}N NMR studies on the en ligand in the Pt(en)X$_n$ system (en = 1,2-diaminoethane; X = Cl, Br, or I) have proved particularly useful and shown that the ^{15}N chemical shift and *J*-coupling values to ^{195}Pt are sensitive probes of the metal oxidation state.[13] Moreover, it was found that the effective oxidation states of the platinum atoms in the monomeric complexes, Pt(en)X$_2$ and Pt(en)X$_4$, do not change significantly on formation of the linear-chain complex, [Pt(en)X$_2$][Pt(en)X$_4$].

One particular topic of interest is the behavior of mixed-valence linear-chain complexes of platinum containing two different bridging halogen atoms.[16−18] Early work on $[\mathrm{Pt(en)_2}][\mathrm{Pt(en)_2X_2}](\mathrm{ClO_4})_4$ complexes containing both chlorine and bromine atoms in bridging positions suggested that these complexes consist of discrete segments of pure $[\mathrm{Pt(en)_2}][\mathrm{Pt(en)_2Cl_2}](\mathrm{ClO_4})_4$ and $[\mathrm{Pt(en)_2}][\mathrm{Pt(en)_2Br_2}](\mathrm{ClO_4})_4$ with only a small number of interfaces between them.[16−19] This claim was based on preliminary resonance Raman results which did not show any peak readily ascribable to Cl−Pt^{IV}−Br units.[18,19] Other workers initially claimed that Cl−Pt^{IV}−Br units are “forbidden

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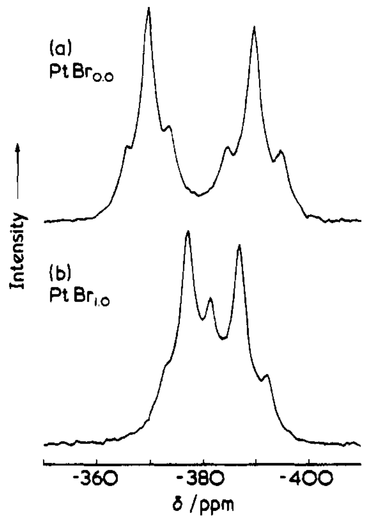

Figure 1. ^{15}N CP/MAS NMR spectra of (a) $[Pt(en)_2][Pt(en)_2Cl_2](ClO_4)_4$ (designated $PtBr_{0.0}$) and (b) $[Pt(en)_2][Pt(en)_2Br_2](ClO_4)_4$ (designated $PtBr_{1.0}$). The spectra were recorded at 45 °C.

because both $[Pt(en)_2]^{2+}$ and $[Pt(en)_2X_2]^{2+}$ ions used in the synthesis are stable in solution";[16,17] however, halogen exchange to form mixed-halogen complexes is known to occur in solution[18,20] and so the presence of such units in the solid state cannot be ruled out on this basis. The length of the postulated discrete segments of chloride and bromide chains is of considerable importance as resonance Raman data on photoexcited or doped samples have been interpreted to suggest that charge separation occurs, with electron polarons more likely to exist in the bromide segments and hole polarons more likely in the chloride segments, leading to potential applications in photovoltaic devices.[21-24] A more recent detailed analysis of the resonance Raman spectra of these complexes, by contrast to earlier ones, has assigned peaks to localized $Br-Pt^{IV}-Cl$ stretching modes and indicated that the length of the bromide-only segments must be small.[25] A structural study of linear-chain platinum complexes containing both chlorine and iodine atoms in bridging positions has also been published.[26]

In view of the potential importance of these materials, we chose to examine the halogen distribution within the chains using high-resolution solid-state NMR spectroscopy in order to complement the results from other structural techniques. In this work, we report ^{15}N NMR results on $[Pt(en)_2][Pt(en)_2Cl_{2-2x}Br_{2x}](ClO_4)_4$ linear-chain complexes (where x denotes the fraction of bromine present, $0 \leq x \leq 1$). For convenience throughout this paper the complexes of this form will be abbreviated as $PtBr_x$. The ^{15}N NMR results give a direct measurement of the disposition around the Pt(IV) sites and show unambiguously that the halogen atom distribution along the chain is close to random.

Results

Figure 1 shows the ^{15}N CP/MAS NMR spectra of the end-members of the series, $PtBr_{0.0}$ and $PtBr_{1.0}$. Two peaks are observed corresponding to ^{15}N bonded to Pt(IV) and Pt(II) sites, together with satellites due to J-coupling to ^{195}Pt (spin $I = {}^1/_2$, 33.8% natural abundance). For the sake of comparison we also measured ^{15}N CP/MAS NMR spectra on monomeric complexes, $Pt(en)_2X_n$. J-coupling values were measured for those samples whose spectral resolution was sufficient for a reliable figure to be obtained by deconvolution. The chemical shifts and J-coupling values are in line with our previous work on $Pt(en)X_n$ complexes[13] and are summarized in Table 1. It is worth noting that the peak due to ^{15}N bonded to Pt(IV) changes frequency significantly on changing the bridging halogen atom from chlorine to bromine, while there is a smaller change in chemical shift for ^{15}N bonded to Pt(II).

It is of interest that two ^{15}N peaks are observed for both $[Pt(en)_2]Cl_2$ and $[Pt(en)_2Cl_2]Cl_2$. This is consistent with the X-ray crystal structure of $[Pt(en)_2]Cl_2$ which shows that there are two nonequivalent nitrogen sites with Pt−N bond distances of 2.039 and 2.046 Å;[27] it seems likely that the en ligands in $[Pt(en)_2Cl_2]Cl_2$ adopt a similar conformation. The chemical shifts for these monomeric complexes are, however, significantly to higher frequency than those observed for similar environments in the $PtBr_x$ complexes. In order to establish the basis for this difference we also measured ^{15}N NMR spectra on the monomeric complexes containing ClO_4^- as the charge-balancing anion rather than Cl^-. These show only a single ^{15}N peak at a chemical shift within about 2 ppm of those observed for the $Cl-Pt-Cl$ environments in the $PtBr_x$ complexes. The single ^{15}N peak is in agreement with the X-ray crystal structure determination of $[Pt(en)_2Cl_2](ClO_4)_4$ which shows that all the nitrogen environments are identical.[28] Hence it is clear that the ^{15}N chemical shift, particularly for ^{15}N bonded to the Pt(II) sites, is quite sensitive to the anion present; this is presumably a reflection of different degrees of hydrogen bonding between the amine and the anion.[3,4] The situation for the bromide monomeric complexes is similar, with chemical shifts being found at higher frequency than those for the linear-chain complexes.

It is known that for the $PtBr_x$ complexes close to room temperature there is a phase transition, the exact temperature of which depends on halogen content.[18] DSC results on our samples show similar trends to those previously reported:[18] the onset of the transition varies roughly linearly with increasing bromine concentration from 18.5 °C for $PtBr_{0.0}$ to 27.2 °C for $PtBr_{1.0}$ with enthalpy changes of between 9.0 and 11.6 kJ mol^{-1}. In order to be confident about the interpretation of the results, the ^{15}N NMR spectra reported here were all recorded at 45 °C (i.e. for the high-temperature phase). In practice it was found that there is negligible difference between these spectra and those recorded at ambient temperature (22 °C); this presumably reflects the fact that the phase transition principally involves changes in the ClO_4^- ion locations with modification to the hydrogen bonding network between chains, rather than to any direct changes to the structure of the chain and/or ligand.[29]

Figure 2 shows the ^{15}N CP/MAS NMR spectra obtained on the mixed-halogen linear-chain complexes, $PtBr_{0.25}$, $PtBr_{0.5}$, and $PtBr_{0.75}$. In the NMR spectrum of $PtBr_{0.25}$ in the region due to ^{15}N bonded to Pt(IV) atoms (the high-frequency side of the spectra), the peak corresponding to $Cl-Pt^{IV}-Cl$ units at −369.5 ppm is still strong but is now accompanied by another peak at −373.3 ppm. This peak has a chemical shift intermediate

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Table 1. Summary of Observed ^{15}N Chemical Shifts (δ/ppm) with $J(^{15}\mathrm{N}-^{195}\mathrm{Pt})$ Coupling Constants in Parentheses (J/Hz)[a]

sample	Cl$-$Pt$^{IV}-$Cl	Br$-$Pt$^{IV}-$Cl	Br$-$Pt$^{IV}-$Br	Br$-$Pt$^{II}-$Br	Br$-$Pt$^{II}-$Cl	Cl$-$Pt$^{II}-$Cl
PtBr$_x$[b]	−369.5 (240)	−373.3	−377.0 (250)	−386.7 (310)	−388.0	−389.6 (300)
[Pt(en)$_2$Cl$_2$]Cl$_2$	−363.2 and −367.2 (250)					
[Pt(en)$_2$Cl$_2$](ClO$_4$)$_2$	−367.5 (235)					
[Pt(en)$_2$]Cl$_2$						−376.9 and −380.2 (300)
[Pt(en)$_2$](ClO$_4$)$_2$						−387.4 (305)
[Pt(en)$_2$Br$_2$]Br$_2$			−371.0			
[Pt(en)$_2$Br$_2$](ClO$_4$)$_2$			−375.0			
[Pt(en)$_2$]Br$_2$				−376.1		

[a] Chemical shift values are accurate within ±0.4 ppm, while spin−spin coupling constants are accurate within ±20 Hz. [b] [Pt(en)$_2$][Pt(en)$_2$Cl$_{2-2x}$Br$_{2x}$](ClO$_4$)$_4$ is abbreviated as PtBr$_x$.

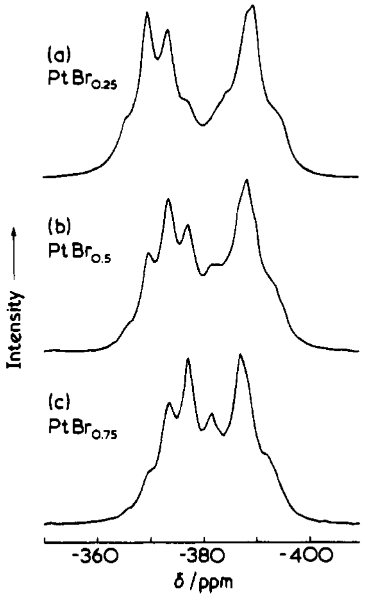

Figure 2. ^{15}N CP/MAS NMR spectra of (a) PtBr$_{0.25}$, (b) PtBr$_{0.5}$, and (c) PtBr$_{1.0}$. The spectra were recorded at 45 °C.

between that of ^{15}N bonded to Cl$-$Pt$^{IV}-$Cl and to Br$-$Pt$^{IV}-$Br units and, therefore, almost certainly reflects the presence of Cl$-$Pt$^{IV}-$Br units. On increase of the bromine concentration to PtBr$_{0.5}$, it is seen that the intensity of the peak due to Cl$-$Pt$^{IV}-$Br units increases, and it is now accompanied by a new peak at −377.0 ppm which corresponds exactly in position to that expected for ^{15}N bonded to Br$-$Pt$^{IV}-$Br units. Similarly on further increasing the bromine concentration to PtBr$_{0.75}$, the peak due to Br$-$Pt$^{IV}-$Br units increases in intensity at the expense of the others. There are also small changes in the region of ^{15}N bonded to Pt(II) species, with a gradual shift from −389.6 for PtBr$_{0.0}$, to −388.0 ppm for PtBr$_{0.5}$, to −386.7 ppm for PtBr$_{1.0}$.

The CP/MAS NMR spectra under these conditions should be quantitative as all the ^{15}N environments in the en ligands are expected to cross-polarize at the same rate. Hence the peak areas will give a reliable measurement of the relative amounts of the different units present. The presence of a strong peak due to ^{15}N bonded to Cl$-$Pt$^{IV}-$Br units contradicts the early suggestions[16−19] that the chains exist as discrete units of [Pt(en)$_2$][Pt(en)$_2$Cl$_2$](ClO$_4$)$_4$ and [Pt(en)$_2$][Pt(en)$_2$Br$_2$](ClO$_4$)$_4$ with only a small number of interfaces between them.

It is necessary to deconvolute the spectra to obtain reliable peak areas, a process which is hindered somewhat by the presence of the J-coupling satellites to ^{195}Pt. However, the J-coupling values (and intensities) are known, and it so happens that in this magnetic field the positions of the J-coupling satellites overlap exactly with the chemical shift of the neighboring X$-$Pt$^{IV}-$X peak. Figure 3 shows the analysis of the sample PtBr$_{0.5}$. The high-frequency part of the spectrum, corresponding to ^{15}N bonded to Pt(IV), was deconvoluted into five peaks (two extreme J-coupling satellites and three main peaks overlapping with J-coupling satellites). Peak overlap within the low-frequency part of the spectrum, corresponding to ^{15}N bonded to Pt(II), is such that a reliable measurement of the different X$-$Pt$^{II}-$X species cannot be obtained, and so this region was simulated using only three peaks (two satellites and the main peak) despite the fact that there is evidence for some fine structure. This analysis (Table 2) provides a measure of the relative proportions of Cl$-$Pt$^{IV}-$Cl, Cl$-$Pt$^{IV}-$Br, and Br$-$Pt$^{IV}-$Br groups. These relative amounts enable the relative halogen concentrations in the chain positions to be calculated. In principle these could differ from those obtained by elemental analysis if there were halogen atoms present in any impurities. However, reasonable agreement was found with the values expected from the quantities of constituents used in the syntheses: the NMR analysis reveals that sample PtBr$_{0.25}$ has 25.5% bromine in the chain, sample PtBr$_{0.5}$ has 53% bromine, and sample PtBr$_{0.75}$ has 77% bromine.

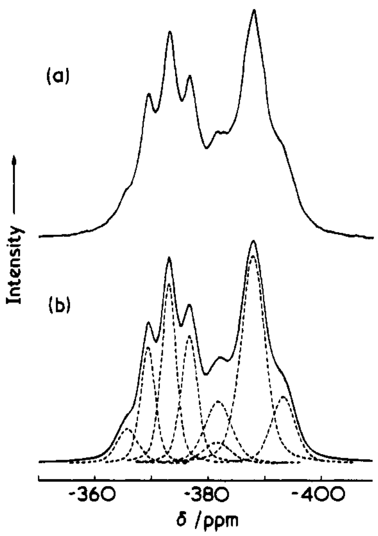

Figure 3. Analysis of the ^{15}N CP/MAS NMR spectrum of PtBr$_{0.5}$: (a) experimental; (b) deconvolution into individual peaks and simulation.

Table 2. Relative Proportions (%) of Pt(IV) Environments[a]

sample	Cl$-$Pt$^{IV}-$Cl	Br$-$Pt$^{IV}-$Cl	Br$-$Pt$^{IV}-$Br
PtBr$_{0.0}$	100		
PtBr$_{0.25}$	59 (56)	31 (38)	10 (7)
PtBr$_{0.5}$	26 (22)	40 (50)	33 (28)
PtBr$_{0.75}$	8 (5)	30 (35)	62 (59)
PtBr$_{1.0}$			100

[a] The parenthetical numbers give the percentage expected on the basis of a random distribution.

Discussion

For a random distribution of halogen atoms bonded to the Pt(IV) sites, the relative intensities of the different units can easily be predicted from probability theory: the relative amounts are expected to be $(1 - x)^2$ for Cl−Pt−Cl units, $2x(1 - x)$ for Cl−Pt−Br units, and x^2 for Br−Pt−Br units, where x is the fraction of bromine present. It is apparent from the deconvoluted areas in Table 1 that there is fair agreement between the values expected on the basis of the random model and the experimental intensities. However, for all three samples the intensities of the Cl−Pt^{IV}−Br units are lower, while those of the Cl−Pt^{IV}−Cl and Br−Pt^{IV}−Br units are somewhat higher, than those expected on the basis of a purely random distribution model. This indicates that there is a slightly greater probability for the occurrence of Cl−Pt^{IV}−Cl and Br−Pt^{IV}−Br units than for the mixed-halogen unit. The NMR spectra allow us to estimate this probability. If we define p(Br/Br) as the probability of Br being bonded to a Pt^{IV} to which one Br is already attached (and employ a similar definition for p(Cl/Cl)), then we can fit the experimental data using the following probabilities:

$x = 0.255$ $p(\mathrm{Br/Br}) = 0.39$ $p(\mathrm{Cl/Cl}) = 0.79$
$x = 0.53$ $p(\mathrm{Br/Br}) = 0.62$ $p(\mathrm{Cl/Cl}) = 0.55$
$x = 0.77$ $p(\mathrm{Br/Br}) = 0.81$ $p(\mathrm{Cl/Cl}) = 0.35$

Hence in all cases the probability of forming the homohalogen unit is slightly greater than the fraction of that halogen present. Note that there is also close agreement between p(Br/Br) and p(Cl/Cl) at equivalent concentrations, indicating that there is no great difference between the preference for forming Br−Pt^{IV}−Br and Cl−Pt^{IV}−Cl units over the mixed-halogen unit.

It is interesting to compare the distribution of halogen atoms in the solid $PtBr_x$ complexes with thermodynamic studies on the conversion of $[Pt(en)_2Cl_2]^{2+}$ to $[Pt(en)_2Br_2]^{2+}$ in solution. Poë found that the ratio, K_1/K_2, of the equilibrium constants for the reactions $[Pt(en)_2Cl_2]^{2+} + Br^- \rightarrow [Pt(en)_2ClBr]^{2+}$ (K_1) and $[Pt(en)_2ClBr]^{2+} + Br^- \rightarrow [Pt(en)_2Br_2]^{2+}$ (K_2) in solution is 2.7 (which may be compared with 4.0 for a random distribution).[20] The effective ratio, K_1/K_2, in the solid $PtBr_x$ complexes calculated using the determined halogen distributions as given in Table 2 is between 1.6 and 1.9, which is only slightly lower than that in solution. This is a significant observation as the growth of $PtBr_x$ crystals would be expected to be additionally affected by kinetic factors and the presence of other ions in solution. The kinetics of the halogen-exchange reaction in solution have also been studied, and it is believed to proceed via a bridging-halogen transition state.[30]

The above NMR results might also be used to predict the average lengths of chloride and bromide units within the chains; this is relevant to the interpretation of resonance Raman data. However, the halogen atoms around the Pt^{II} atoms are even more likely to be randomly distributed than those, more closely bonded, to the Pt^{IV} atoms (though this information is not available directly from the NMR spectra due to lack of resolution in the region of ^{15}N bonded to Pt(II) atoms). Taking this fact into consideration, together with the significant amount of mixed-halogen species at the Pt(IV) sites, it thus seems highly probable that the overall distribution of halogen atoms within the chain can, to a first approximation at least, be treated as essentially random. It is interesting to note that the results are very similar to those found for certain other systems containing mixed-halogen atoms, such as the $TiCl_4/TiBr_4$ and $SnCl_4/SnBr_4$ mixtures.[31]

Conclusions

High-resolution solid-state ^{15}N NMR spectroscopy is a powerful tool with which to determine local ordering in linear-chain complexes of platinum containing a mixture of halogen atoms. The results show that the halogen distribution is close to random. This information is important in considering applications of these materials and in interpreting data on these complexes obtained via other techniques of characterization.

Experimental Section

Sample Preparation. It was found that the monomeric complexes prepared according to standard procedures given in the literature showed impurity peaks in the solid-state ^{15}N NMR spectra, and for this reason the preparation of the pure complexes is described in detail:

$[Pt(en)_2]Cl_2$. A solution containing equimolar amounts of K_2PtCl_4 and ^{15}N-enriched en·2HCl was held under reflux at 90 °C and treated with 2 molar equiv of NaOH. The hot, pale yellow solution was then treated with sufficient free unenriched en to decolorize it. The resulting $[Pt(en)_2]^{2+}$ ions were then extracted by addition of $[PtCl_4]^{2-}$ solution to form $[Pt(en)_2][PtCl_4]$, whose purity was checked by elemental analysis and solid-state ^{15}N NMR spectroscopy. The pink $[Pt(en)_2][PtCl_4]$ was then suspended in water, held under reflux at 90 °C, and treated fully with further free unenriched diamine. The colorless solution was then reduced in volume, cooled, and filtered to remove any $Pt(en)Cl_2$. The filtrate was reduced still further and the desired product extracted by addition of ethanol and then recrystallized from an ethanol/water mixture.

$[Pt(en)_2](ClO_4)_2$. This was produced from $[Pt(en)_2]Cl_2$ by successive treatments with perchloric acid (5 molar equivs) and extractions until the solid-state ^{15}N NMR spectrum showed only pure $[Pt(en)_2](ClO_4)_2$ to be present. Three recrystallizations were required to ensure complete conversion. Note that if too much acid is used, or the solution left too long before extraction, then oxidation to the linear-chain complex can occur. A ^{15}N NMR spectrum of an intermediate product showed a peak that suggested the presence of $[Pt(en)_2](Cl)(ClO_4)$.

$[Pt(en)_2Cl_2](ClO_4)_2$. This was reliably prepared by oxidation of $[Pt(en)_2](ClO_4)_2$ using chlorine in dilute perchloric acid. An alternative preparative route involving treatment of $[Pt(en)_2Cl_2]Cl_2$ with perchloric acid was found to give a mixture of the desired product and the linear-chain complex (which could then be further oxidized to the desired product).

$[Pt(en)_2Br_2](ClO_4)_2$. This was prepared by direct bromination of $[Pt(en)_2](ClO_4)_2$ but required stronger reaction conditions (heat, reaction time) than for the analogous chlorination to produce $[Pt(en)_2Cl_2](ClO_4)_2$ and also required careful recrystallization to ensure a pure product.

$[Pt(en)_2][Pt(en)_2Cl_{2-2x}Br_{2x}](ClO_4)_4$ (abbreviated as $PtBr_x$ throughout this paper). The chloride linear-chain complex, $PtBr_{0.0}$, was prepared by mixing $[Pt(en)_2](ClO_4)_2$ and $[Pt(en)_2Cl_2](ClO_4)_4$ in equimolar amounts in dilute perchloric acid and allowing the mixture to crystallize. Similarly, the bromide complex $PtBr_{1.0}$ was prepared from $[Pt(en)_2](ClO_4)_2$ and $[Pt(en)_2Br_2](ClO_4)_4$. The mixed-halogen complexes, with nominal compositions $PtBr_{0.25}$, $PtBr_{0.5}$, and $PtBr_{0.75}$, were prepared simply by mixing the required amounts of $PtBr_{0.0}$ and $PtBr_{1.0}$ in dilute perchloric acid and allowing the product to crystallize over at least 16 h. Elemental analysis of the product revealed that the halogen concentration was close to that expected on the basis of the stoichiometry of the starting materials [found, % (predicted, %)]:

$PtBr_{0.0}$	Cl: 19.8 (19.3)	Br: 0.2 (0.0)
$PtBr_{0.25}$	Cl: 17.2 (17.4)	Br: 4.1 (3.6)
$PtBr_{0.5}$	Cl: 15.7 (15.6)	Br: 7.0 (7.0)
$PtBr_{0.75}$	Cl: 14.1 (13.7)	Br: 10.4 (10.3)
$PtBr_{1.0}$	Cl: 12.2 (12.0)	Br: 13.5 (13.4)

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Electron microprobe analysis was used to check the homogeneity of the samples: it was found that a substantial majority of the crystals within each sample had almost identical chemical compositions and that there were only a few crystals which had significantly different compositions from that of the bulk. Similar conclusions were drawn from Raman spectra of single crystals recorded using a Dilor XY Raman microscope.

Solid-State NMR. ^{15}N solid-state NMR spectra were recorded using a Bruker MSL-300 spectrometer at 30.42 MHz using cross-polarization (CP), proton dipolar decoupling, and magic-angle spinning (MAS). The cross-polarization condition was set on a sample of doubly ^{15}N-enriched ammonium nitrate. A spinning speed of 4 kHz was employed; this is sufficient to eliminate all spinning sidebands for these complexes. A contact time of 0.5 ms was used with a typical recycle delay between scans of 5 s. The acquisition time was normally 30 ms. The 90° pulse length for protons during cross-polarization was 7 μs, while the proton decoupling power during acquisition was increased to be equivalent to a 90° pulse length of 3.75 μs. Due to a phase transition which is known to occur close to room temperature for these complexes, all spectra were recorded at 45 °C (above the transition temperature). Chemical shifts are quoted relative to external liquid nitromethane using solid ammonium nitrate as a secondary reference: the ammonium peak was taken to resonate at −358.4 ppm.[32]

Differential Scanning Calorimetry. DSC experiments were made by a Perkin-Elmer DSC7 on approximately 10 mg of sample placed on an aluminium crucible in a nitrogen atmosphere using a heating rate of 5 °C/min.

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