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# $^{15}N$ Solid-State NMR Study of Ligands in Platinum Mixed-Valence Complexes

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$^{15}N$ solid-state NMR spectra have been recorded on a series of platinum complexes with two different amine ligands, $^{15}N$-enriched 1,2-diaminoethane (en) and natural abundance 3,7-diazanonane-1,9-diamine (2,3,2-tet). The results show that the $^{15}N$ chemical shift and $J$ coupling to $^{195}Pt$ are very sensitive to the effective oxidation state of the metal atom and that, in both discrete platinum(II) and platinum(IV) complexes as well as in mixed-valence complexes which can be formed therefrom, the platinum atom environments become more similar on changing from a chloro to a bromo to an iodo species. This trend is attributable to the fall in the electronegativity of the halogen atom (Cl > Br > I) and thus to a lowering of the effective positive charge on the metal atom as the halogen atom is changed in this order, and not to increased valence delocalization upon formation of a linear chain.

## Introduction

A large number of halogen-bridged linear-chain complexes of nickel, palladium, and platinum, of interest due to their highly anisotropic optical and conductivity properties, have now been synthesized and characterized by a variety of techniques.[1] These complexes, as typified by Wolffram's red, $[Pt^{II}(NH_2Et)_4][Pt^{IV}(NH_2Et)_4Cl_2]Cl_4\cdot 4H_2O$, are mixed-valent with the general structure represented in Figure 1a. This structure can be considered as a Peierls-distorted version of a symmetric one, with a short $M^{IV}$–X distance and a long $M^{II}$–X one. However, there is a variety of evidence suggesting that valence delocalization occurs on formation of these materials. Structural analyses of a wide range of complexes indicate that the average ratio of the $M^{IV}$–X to $M^{II}$–X distance is 0.75, 0.79, and 0.88 for X = Cl, Br, and I, respectively,[2] suggesting increased valence delocalization in the order Cl < Br < I. Hence the oxidation state of the metal atom may better be described as $M^{II+\alpha}$ and $M^{IV-\alpha}$ where the degree of partial oxidation, $\alpha$, lies between 0 and 1. Indeed, a nickel complex has recently been discovered in which the halogen is equidistant between the metal centers, implying that $\alpha = 1$ and that the complex contains a nickel(III) chain.[3] The conductivity of these complexes in the chain direction, $\sigma_{\parallel}$, is greater the nearer the bridging atom is to the central position, as made evident by the fact that $\sigma_{\parallel}$ increases by ca. $10^4$ on changing from chlorine- to analogous bromine-bridged complexes, and by a further similar factor on changing from bromine- to analogous iodine-bridged complexes.[4] Moreover, a shift to lower wavenumber of the intervalence (IVCT) band, $M^{II+\alpha} \rightarrow M^{IV-\alpha}$, takes place in the order Cl > Br > I[1,2], consistent with the increase in $\alpha$ in this order.

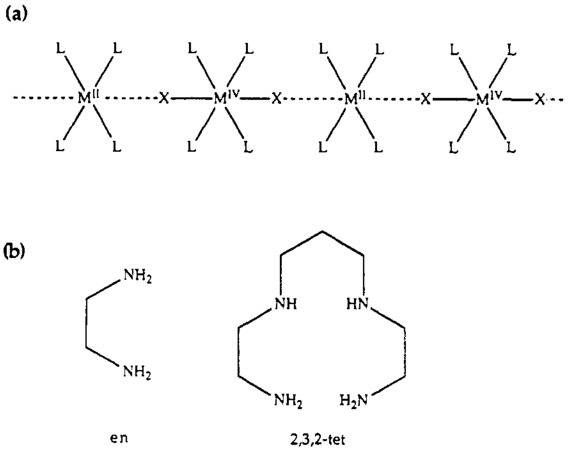

**Figure 1.** (a) Representation of a linear-chain mixed-valence complex. M is nickel, palladium, or platinum, X is chlorine, bromine, or iodine, and L is a monodentate ligand. (b) Structures of 1,2-diaminoethane (en) and 3,7-diazanonane-1,9-diamine (2,3,2-tet).

In this paper we report detailed $^{15}N$ solid-state NMR measurements on two amine ligands in complexes of platinum(II) and of platinum(IV), and in platinum mixed-valence linear-chain species. Solution $^{15}N$ NMR spectroscopy is an excellent routine probe of nitrogen environment, but these complexes are either insoluble or decompose on dissolution, thus necessitating the use of solid-state NMR techniques (magic-angle spinning, MAS, and high power proton decoupling). While $^{15}N$ has a low natural abundance (0.37%) and low sensitivity (ca. $10^{-3}$ times that of a proton) and so is difficult to detect, the use of cross-polarization (CP) in the solid state when there are nearby protons available can enable reasonable quality spectra to be obtained even at natural abundance. High quality spectra can be obtained easily with a degree of $^{15}N$ isotopic enrichment, as have been reported for $Pt(NH_3)_2(SCN)_2$ by Santos et al.[5] $^{13}C$ CP/MAS NMR spectra have previously been reported for various ligands in mixed-valence nickel and palladium complexes,[6] but it is expected that $^{15}N$ NMR should prove to be a far more sensitive probe of the metal oxidation state, since the nitrogen atoms are directly bonded to the metal atoms. Further, in the case of bonding to platinum, there is the chance of detecting $J$ coupling between $^{15}N$ and $^{195}Pt$ ($I = {}^1/_2$, 33.8% abundance). The direct use of $^{195}Pt$ MAS NMR is also a possibility but is hindered by the extremely large chemical shift anisotropy of the platinum atom environment in these materials (up to several thousand ppm), necessitating the use of extremely fast spinning speeds in order to achieve good quality spectra.[7,8] In this paper we use $^{15}N$-enriched 1,2-diaminoethane (en), a bidentate ligand, to demonstrate initially

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(1) Clark, R. J. H. *Chem. Soc. Rev.* **1984**, *13*, 219; **1990**, *19*, 107.

(2) Clark, R. J. H. *Advances in Infrared and Raman Spectroscopy*; Clark, R. J. H., Hester, R. E., Eds.; Wiley: Chichester, U.K., 1984, Vol. 11, p 95.

(3) Toriumi, K.; Okamoto, H.; Mitani, T.; Bandow, S.; Yamashita, M.; Fujii, Y.; Clark, R. J. H.; Michael, D. J.; Edwards, A. J.; Watkin, D.; Kurmoo, M.; Day, P. *Mol. Cryst. Liq. Cryst.* **1990**, *181*, 333.

(4) Hamaue, Y.; Aoki, R.; Yamashita, M.; Kida, S. *Inorg. Chim. Acta* **1981**, *54*, L13.

(5) Santos, R. A.; Chien, W.-J.; Harbison, G. S.; McCurry, J. D.; Roberts, J. E. *J. Magn. Reson.* **1989**, *84*, 357.

(6) Ikeda, R.; Tamura, T.; Yamashita, M. *Chem. Phys. Lett.* **1990**, *173*, 466.

(7) Sparks, S. W.; Ellis, P. D. *J. Am. Chem. Soc.* **1986**, *108*, 3215.

(8) Austin, E. J. W.; Barrie, P. J.; Clark, R. J. H. Unpublished work.

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that useful structural information on these complexes can be obtained from $^{15}N$ solid-state NMR spectra, and then we extend the study to natural abundance $^{15}N$ spectra of complexes of a quadridentate ligand, 3,7-diazanonane-1,9-diamine[9] (here denoted as 2,3,2-tet), (see Figure 1b).

## Experimental Section

**Sample Preparation. (a) 1,2-Diaminoethane (en) Complexes.** Doubly $^{15}N$-enriched 1,2-diaminoethane dihydrogen chloride (99 atom % from MSD isotopes) was used as the source of $^{15}N$ nuclei.

**(i) Platinum(II) Monomers.** $Pt(en)Cl_2$ was prepared by a standard route.[10] This was enriched to approximately 25% by treating fully 4 equiv of potassium tetrachloroplatinate with 1 equiv of fully enriched en·2HCl prior to treating with a further 3 equiv of an unenriched sample of en·2HCl. $Pt(en)I_2$ was synthesized from $Pt(en)Cl_2$ using the method of Watt and McCarley.[11] $Pt(en)Br_2$ was prepared both from an adaptation of Johnson's method[10] and $K_2PtBr_4$, and from $Pt(en)Cl_2$ treated with KBr.[11]

**(ii) Platinum Linear-Chain Complexes.** $[Pt(en)Cl_2][Pt(en)Cl_4]$ was made by an adaptation of the method of Chugaev and Chernyaev,[12] half the specified amount of persulfate being used. The linear-chain bromide and iodide were synthesized by an analogous route. All these complexes were also prepared by treating equimolar amounts of platinum(II) and platinum(IV) complexes in the presence of the corresponding halide acid.

**(iii) Platinum(IV) Monomers.** $Pt(en)Cl_4$ was prepared from $Pt(en)Cl_2$ by the chlorine oxidation method of Basolo et al.[13] $Pt(en)Br_4$ and $Pt(en)I_4$ were prepared initially by the oxidation of the corresponding $Pt(en)X_2$ compounds using conditions similar to those of Chugaev and Chernyaev,[12] with double the amount of persulfate and free halide. Platinum(IV) complexes were also subsequently made using methods similar to those outlined above, but with the linear-chain complexes as starting materials.

**(b) 3,7-Diazanonane-1,9-diamine (2,3,2-tet) Complexes.** $[Pt(2,3,2\text{-}tet)]Cl_2$ was prepared by heating to 90 °C a stirred solution containing potassium tetrachloroplatinate and a slight excess of amine. The reaction proceeded via the insoluble intermediate $[Pt(2,3,2\text{-}tet)][PtCl_4]$ to a colorless solution. The product was recovered by evaporating the solution to minimum volume and was then recrystallized from water. $[Pt(2,3,2\text{-}tet)Cl_2]Cl_2$ was made by a standard oxidation method.[13] Linear-chain complexes were synthesized[9] by methods analogous to those of Bekaroglu et al.,[14] employing the starting materials indicated above.

**Solid-State NMR.** $^{15}N$ solid-state NMR spectra were recorded using a Bruker MSL-300 spectrometer at 30.42 MHz using cross-polarization, proton dipolar decoupling, and magic-angle spinning. The cross-polarization condition was set on a sample of doubly $^{15}N$-enriched ammonium nitrate. Spinning speeds of 3.5–4.5 kHz were employed, which is sufficient to eliminate virtually all spinning sidebands for these complexes. For the en complexes a contact time of 0.5 ms was used, while for 2,3,2-tet the contact time was 1–10 ms. Acquisition times were typically 40–100 ms, and the recycle delay between scans was between 1 and 8 s. The typical 90° pulse length for protons was 7 μs. In some instances a higher decoupling power was used equivalent to a 90° pulse length of 3.75 μs during the acquisition period to reduce line widths. All spectra were recorded at room temperature (296 K). For the en samples, spectra were obtained with up to 1 h of accumulation time on $^{15}N$ isotopically enriched samples (25–100% enrichment, 40–100 mg quantity). The 2,3,2-tet samples were recorded on 150–300 mg of natural abundance material over 16–60 h. Chemical shifts are quoted relative to external liquid nitromethane using solid $NH_4NO_3$ as a secondary reference: the ammonium peak was taken to resonate at −358.4 ppm.[15] Note that a variety of different reference materials for $^{15}N$ have been used in the literature and that the resonance positions of ammonium peaks (themselves a common reference) in solids are highly dependent on the anion present.[16]

**Table I.** Summary of $^{15}N$ Solid-State NMR Results for $^{15}N$-Enriched $Pt(en)X_n$ Ccomplexes[a]

| | N-Pt(II) | | N-Pt(IV) | |
|---|---|---|---|---|
| compd | δ/ppm | J/Hz | δ/ppm | J/Hz |
| $Pt(en)Cl_2$ | −382.8 | 390 | | |
| $Pt(en)Cl_4$ | | | −355.9 | 260 |
| $[Pt(en)Cl_2][Pt(en)Cl_4]$ | −384.2 | 350 | −357.3 | 250 |
| $Pt(en)Br_2$ | −376.7 | 335 | | |
| $Pt(en)Br_4$ | | | −360.0 | 240 |
| $[Pt(en)Br_2][Pt(en)Br_4]$ | −377.8 | 325 | −362.1 | 245 |
| $Pt(en)I_2$ | −366.2 | | | |
| $Pt(en)I_4$ | | | −368.9 | |
| $[Pt(en)I_2][Pt(en)I_4]$ | −369.5 | | −371.0 | |

[a] Chemical shifts are accurate to within ±0.3 ppm, while the estimated error in the J couplings quoted is ±15 Hz, apart from the case of $Pt(en)Br_2$ for which it is ±50 Hz.

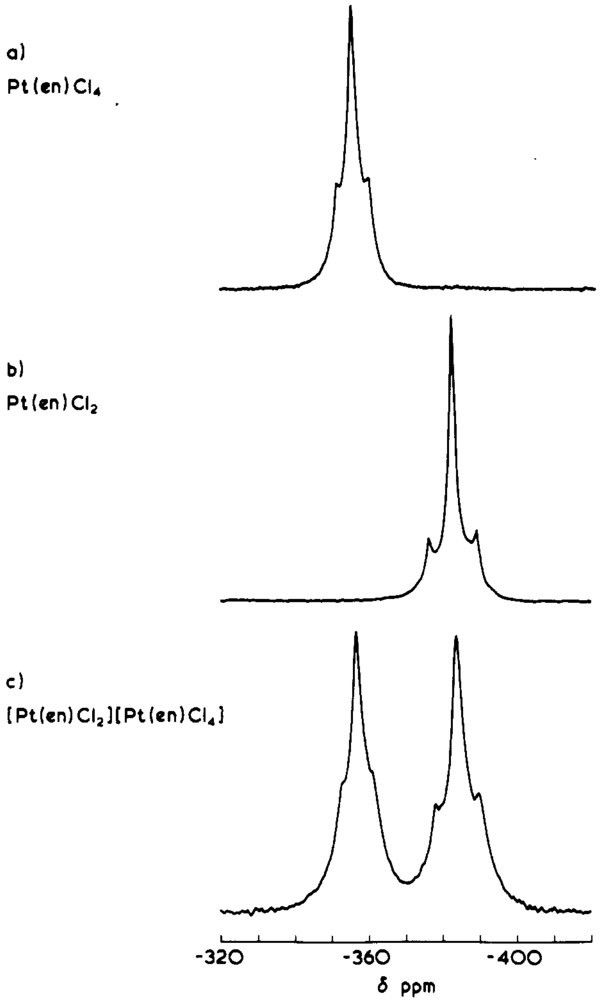

**Figure 2.** Enriched $^{15}N$ CP/MAS NMR spectra of (a) $Pt(en)Cl_4$, (b) $Pt(en)Cl_2$, and (c) $[Pt(en)Cl_2][Pt(en)Cl_4]$.

The observed chemical shifts were not corrected for the changes in magnetic susceptibility between samples.

## Results and Discussion

**1,2-Diaminoethane (en) Complexes.** The $^{15}N$ results obtained for all the $Pt(en)X_n$ (X = Cl, Br, I; n = 2, 3, 4) samples are summarized in Table I. A single $^{15}N$ peak is observed for $Pt(en)Cl_4$ and $Pt(en)Cl_2$ (Figure 2a,b) with satellites due to $^{15}N$–$^{195}Pt$ J coupling, indicating direct nitrogen-to-platinum bonding. The satellite intensities agree well with the expected value: $^{195}Pt$ (spin $I = {}^1/_2$) is 33.8% naturally abundant, and the satellite peaks make up about one-third of the total intensity. It is immediately apparent that both the chemical shift and J coupling are affected by the platinum oxidation state. The J couplings (Table I) are

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(9) Clark, R. J. H.; Michael, D. J.; Yamashita, M. *J. Chem. Soc., Dalton Trans.* **1991**, 725.
(10) Johnson, G. L. *Inorg. Synth.* **1966**, *8*, 242.
(11) Watt, G. W.; McCarley, R. E. *J. Am. Chem. Soc.* **1957**, *79*, 3315.
(12) Chugaev, L.; Chernyaev, J. *Z. Anorg. Allg. Chem.* **1929**, *182*, 159.
(13) Basolo, F.; Bailar, J. C.; Tarr, B. R. *J. Am. Chem. Soc.* **1950**, *72*, 2433.
(14) Bekaroglu, Ö.; Breer, H.; Endres, H.; Keller, H. J.; Nam Gung, H. *Inorg. Chim. Acta* **1977**, *21*, 183.
(15) Witanowski, M.; Stefaniak, L.; Webb, G. A. *Annu. Rep. NMR Spectrosc.* **1986**, *18*, 1.
(16) Ratcliffe, C. I.; Ripmeester, J. A.; Tse, J. S. *Chem. Phys. Lett.* **1983**, *99*, 177.

**Table II.** Summary of Natural Abundance $^{15}N$ Solid-State NMR Results for Pt(2,3,2-tet) Complexes[a]

| | Pt(II)–NH$_2$ | | Pt(II)–NHR | | Pt(IV)–NH$_2$ | | Pt(IV)–NHR | |
|---|---|---|---|---|---|---|---|---|
| compd | $\delta$/ppm | $J$/Hz | $\delta$/ppm | $J$/Hz | $\delta$/ppm | $J$/Hz | $\delta$/ppm | $J$/Hz |
| [Pt(2,3,2-tet)]Cl$_2$ | –382.6 | 310 | –362.5 | 315 | | | | |
| [Pt(2,3,2-tet)Cl$_2$]Cl$_2$ | | | | | –368.7 | 230 | –343.4 | 225 |
| [Pt(2,3,2-tet)][Pt(2,3,2-tet)Cl$_2$](ClO$_4$)$_4$ | –389.6 | 305 | –364.7 | 330 | –372.5 | 230 | –344.3 | 245 |
| [Pt(2,3,2-tet)][Pt(2,3,2-tet)Br$_2$](ClO$_4$)$_4$ | –386.3 | | –360.2 | 335 | –378.4 | | –348.9 | |
| [Pt(2,3,2-tet)][Pt(2,3,2-tet)I$_2$](ClO$_4$)$_4$ | –390.9 | | –358.8 | 310 | –387.1 | | (–358.8) | |

[a] Chemical shifts are accurate within ±0.5 ppm, while the estimated error in the $J$ couplings quoted is ±20 Hz. For the bromo and particularly the iodo samples, the assignment is only tentative owing to peak overlap.

within the expected range of values: in solution for diamine complexes, $^{15}N$–$^{195}Pt$ $J$ couplings lie in the region 247–275 Hz for coupling to Pt(IV) and 302–411 Hz for coupling to Pt(II).[17] Thus both the $^{15}N$ chemical shift and the $J$ couplings appear to be excellent probes of platinum oxidation state. The $^{15}N$ spectrum (Figure 2c) of the mixed-valence complex [Pt(en)Cl$_2$][Pt(en)Cl$_4$] is best described as a superposition of the spectra of the individual components, with only a small change in chemical shift position for each peak (1.4 ppm) on chain formation. Surprisingly, the separation of the peaks is identical to that for the individual monomeric species; this suggests that no change in the effective positive charge on platinum has occurred in these species on their being linked to form a linear chain; i.e., no further change in apparent oxidation state of platinum occurs on chain formation from that which had already taken place on formation of the discrete monomeric complexes. The $J$ couplings (Table I) are also well within the individual ranges for coupling to discrete Pt(IV) and Pt(II) centers.

Similar results are obtained for the Pt(en)Br$_n$ and Pt(en)I$_n$ complexes. The spectra of the mixed-valence complexes are again superpositions of the spectra of the individual Pt(en)X$_2$ and Pt(en)X$_4$ components, with there being only a small change in the chemical shifts on chain formation (Figure 3 and Table I). However, the separation between the $^{15}N$ peaks assigned to nitrogen bonded to Pt(II) and to Pt(IV) in the mixed-valence chains falls from 26.9 ppm (X = Cl) to 15.7 ppm (X = Br) to 1.5 ppm (X = I). While this might seem at first sight to support the concept of increased valence delocalization on chain formation in the order Cl < Br < I, there is no significant decrease in the separation between the resonances attributed to the nitrogen bonded to Pt(II) and to Pt(IV) in the mixed-valence chain from those found for the discrete monomeric species (see Table I). Further, the $J$ couplings observed for the Cl and Br samples remain characteristic of bonding to discrete Pt(II) and Pt(IV) centers. It was not possible to measure $J$ couplings for the iodide samples accurately due to the line widths caused by the effect of residual $^{15}N$–X dipolar interactions. These interactions are not completely removed by MAS, as the Cl, Br, and I isotopes are quadrupolar, and the resulting residual broadening increases as X goes from Cl to Br to I.[18] It is possible that anisotropic susceptibility effects also contribute to the observed linewidths.

The $^{15}N$ chemical shift is determined principally by the shielding of the nucleus by the surrounding electrons, and these results indicate that, for the en complexes, this is more affected by the type of halogen bound to the platinum than by the formation of a linear-chain complex involving possible charge delocalization. Indeed, in the case of Pt(en)I$_2$ and Pt(en)I$_4$ the observed resonances are the other way around from that expected, indicating that the Pt(IV) site is in fact better shielded than the Pt(II) site.

**3,7-Diazanonane-1,9-diamine (2,3,2-tet) Complexes.** To test this result more generally complexes of the 2,3,2-tet ligand were investigated, for which it was considered that the $^{15}N$ chemical shift might show less halogen dependence than for en complexes; this was because the former complexes, being quadridentate, have no halogen atoms in the plane of the $^{15}N$ under investigation.

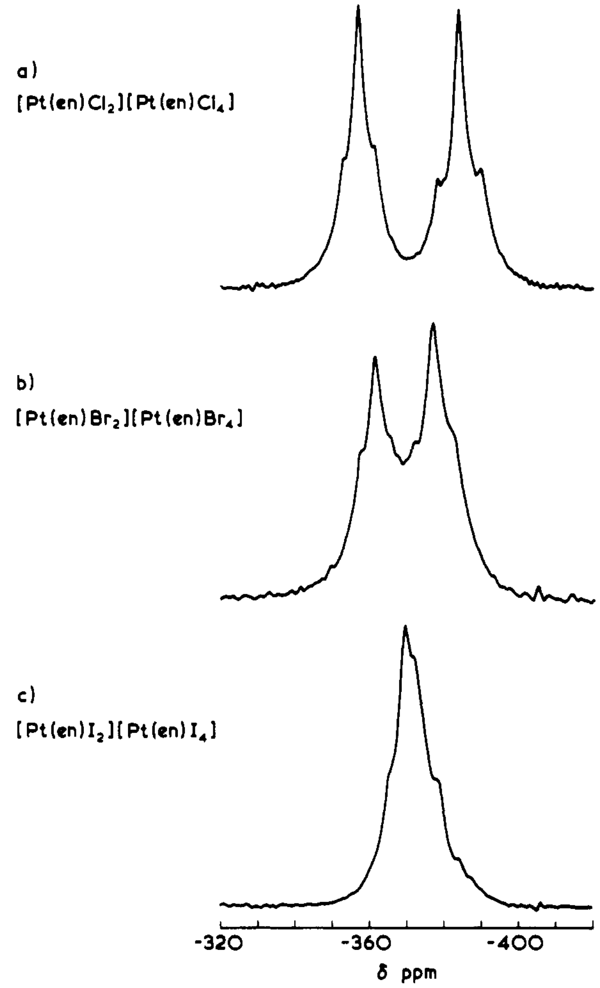

**Figure 3.** Enriched $^{15}N$ CP/MAS NMR spectra of (a) [Pt(en)Cl$_2$][Pt(en)Cl$_4$], (b) [Pt(en)Br$_2$][Pt(en)Br$_4$], and (c) [Pt(en)I$_2$][Pt(en)I$_4$].

Figure 4 shows the $^{15}N$ spectra of [Pt(2,3,2-tet)Cl$_2$]Cl$_2$, [Pt(2,3,2-tet)]Cl$_2$, and the mixed-valence complex [Pt(2,3,2-tet)][Pt(2,3,2-tet)Cl$_2$](ClO$_4$)$_4$. Results on the 2,3,2-tet complexes are summarized in Table II. Despite the fact that the spectra were recorded using natural $^{15}N$ abundance, acceptable spectra were obtained, which again yielded chemical shift and $J$ coupling data. The $J$ couplings are particularly useful in assigning the spectral peaks of the mixed-valence complex unambiguously since they clearly enable a distinction to be drawn between $^{15}N$ bonded to Pt(II) and to Pt(IV) centers.

Two peaks are observed for each 2,3,2-tet ligand bonded to each distinct platinum atom corresponding to the –NH$_2$ and –NHR entities. These may be compared with the chemical shifts in solution for the closely related (H$_2$NCH$_2$CH$_2$NHCH$_2$)$_2$ molecule (2,2,2-tet) which occur at –359.6 ppm (for the –NH$_2$ resonance) and –346.8 ppm (for the –NH one).[15] It is also noticeable that the peaks due to –NH$_2$ signals are slightly broader than those for –NH species. This is possibly due to residual dipolar coupling to protons, though the –NH$_2$ signals remain

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(17) Pregosin, P. *Annu. Rep. NMR Spectrosc.* **1986**, *17*, 285.
(18) Menger, E. M.; Veeman, W. S. *J. Magn. Reson.* **1982**, *46*, 257.

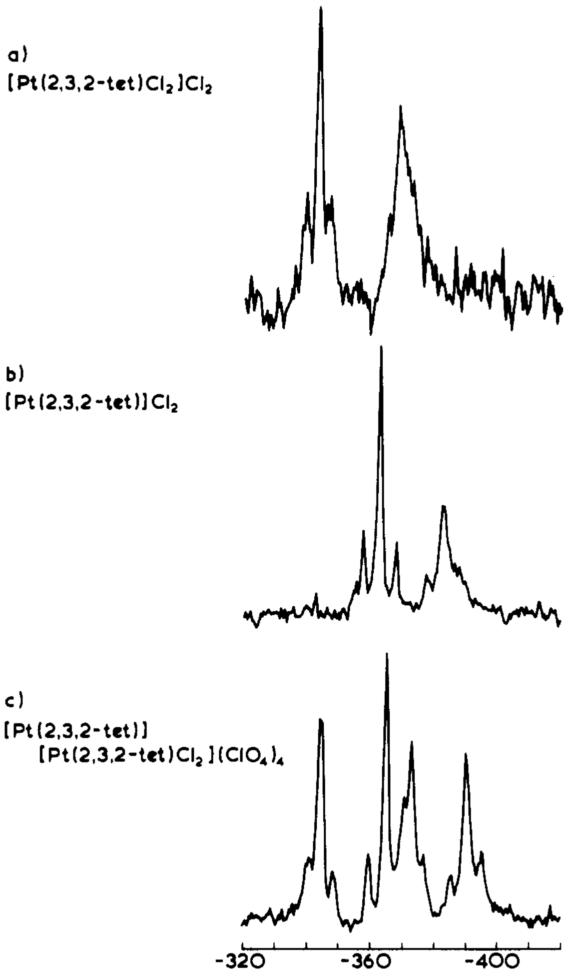

**Figure 4.** Natural abundance $^{15}N$ CP/MAS NMR spectra of (a) [Pt(2,3,2-tet)$Cl_2$]$Cl_2$, (b) [Pt(2,3,2-tet)]$Cl_2$, and (c) [Pt(2,3,2-tet)][Pt(2,3,2-tet)$Cl_2$]$(ClO_4)_4$.

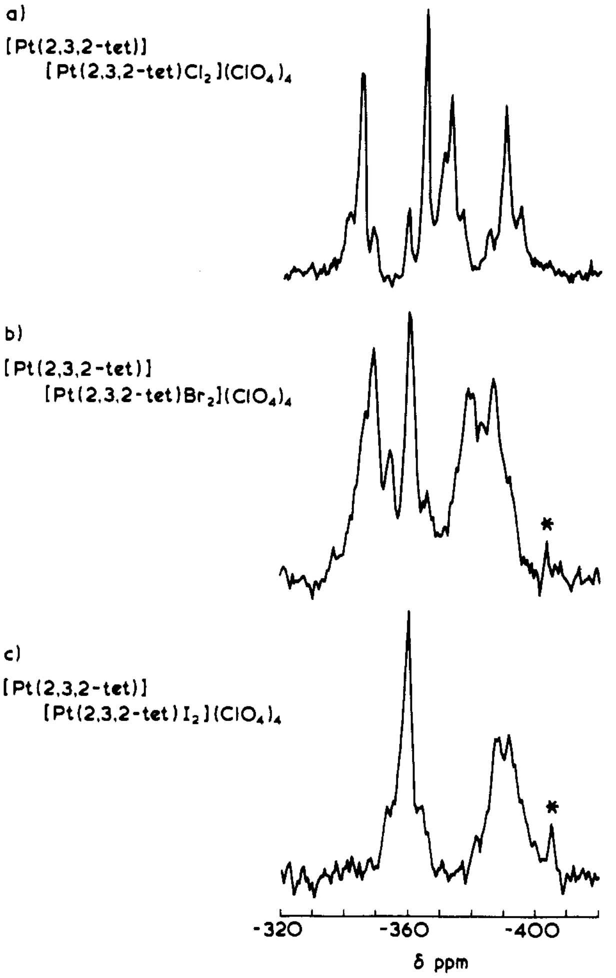

**Figure 5.** Natural abundance $^{15}N$ CP/MAS NMR spectra of (a) [Pt(2,3,2-tet)][Pt(2,3,2-tet)$Cl_2$]$(ClO_4)_4$, (b) [Pt(2,3,2-tet)][Pt(2,3,2-tet)$Br_2$]$(ClO_4)_4$, and (c) [Pt(2,3,2-tet)][Pt(2,3,2-tet)$I_2$]$(ClO_4)_4$. (The "peaks" marked by asterisks are of instrumental origin.)

broader even when the proton decoupling power is increased during the acquisition period to be equivalent to a 90° pulse length of 3.75 μs. The intensities of the *J*-coupled satellites confirm that all four amine groups in the ligand are bonded directly to the platinum center. As observed in the case of the en samples discussed above, there is a change in resonance position for $^{15}N$ bonded to Pt(IV) as compared to Pt(II). Thus once again the $^{15}N$ chemical shift seems to be a good indicator of platinum oxidation state, though the difference between the resonance positions for $^{15}N$ bonded to Pt(IV) and to Pt(II) is not identical for the $-NH_2$ and –NH groups. As in the en ligand case discussed above, the spectrum of the mixed-valence complex can be considered to be a superposition of the spectra of the two individual components, with comparatively small changes in chemical shift on formation of the chain complex. In this case, however, the difference in chemical shift between $^{15}N$ bonded to Pt(II) and to Pt(IV) has in fact increased slightly in the mixed-valence complex compared to that for the discrete monomers. The lack of any decrease suggests that no significant change in degree of partial oxidation has occurred on chain formation; the small increase in chemical shift difference is attributed to the effect of the charge-balancing anion, $ClO_4^-$, in the mixed-valence complex which influences the $^{15}N$ shift through hydrogen-bonding interactions to the –NH and $-NH_2$ hydrogen atoms.

Figure 5 shows the spectra obtained on the bromine- and iodine-bridged analogue of the mixed-valence 2,3,2-tet complex. Unfortunately due to greater peak overlap it is not possible to obtain full *J*-coupling data for these complexes, so the peak assignment (Table II) is rather tentative. The general trend (as for the en complexes above) is that the peaks due to $^{15}N$ bonded to Pt(II) and to Pt(IV) move closer together as Cl → Br → I. This trend is evident in results on both the en and the 2,3,2-tet samples and is thought to be due more to the different properties of the bridging halogens (such as electronegativity and steric effects) on the electronic shielding of the $^{15}N$ nucleus than to any suggested changes in the effective oxidative state of the platinum on chain formation from discrete monomeric platinum(II) and platinum(IV) entities.

**General Discussion.** The physical properties of linear-chain complexes of the platinum group metals have often been discussed in terms of the known variation in the ratio of $M^{IV}$–X to $M^{II}$–X distances. The halogen atom is much nearer to being centrally placed in the case of an iodine-bridged than a bromine- or chlorine-bridged species, and this feature is undoubtedly responsible for the vastly higher chain conductivities of chain species involving the heavier halogens. This halogen dependence is borne out in the NMR results observed here, in which the separation of the $^{15}N$ resonance position for ligands bonded to platinum(II) and platinum(IV) centers decreases in the order Cl > Br > I.

Curiously, however, the $Pt^{IV}$–X distances in cationic or neutral chain complexes (the average values for which are 2.31, 2.50, and 2.74 Å for X = Cl, Br, or I, respectively[2]) are little different from those of analogous discrete platinum(IV) complexes. Moreover, the $Pt^{II}$–X distances in the cationic or neutral chain complexes are all identical (3.05 Å) within about 0.1 Å, irrespective of the bridging halogen atom. Thus the act of chain formation from discrete platinum(II) and platinum(IV) entities does not significantly alter either typical bond lengths or, by implication, the effective positive charges on each metal atom. This latter point has been demonstrated strikingly by the present NMR experiments, on the basis of which it is very clear that there is little, if any, difference between the electronic shielding of the $^{15}$N nucleus in discrete platinum(II) complexes and that in the same entities as they exist in a linear chain, and between the analogous shielding in discrete platinum(IV) complexes and that in the same entitites as they exist in a linear chain.

Most of the other techniques extensively used to study linear-chain complexes (electronic and resonance Raman spectroscopy, electrical conductivity, etc.) are specifically concerned with chain properties, rather than with the local properties probed by NMR spectroscopy. Thus the resonance Raman spectra are concerned with the probing of the nature and magnitude of the geometric change along the $Pt^{IV}$–X direction on excitation to the intervalence state,[19] the IVCT transition ($Pt^{II} \rightarrow Pt^{IV}$) being axially polarized. The chain conductivity is concerned with axial ($Pt^{II} \rightarrow Pt^{IV}$) hopping or band processes and is obviously facilitated by near central bridging of the halogen atom. Indeed, it is simply the act of chain formation which opens up the facile route (the chain direction) for conductivity, thus making the chain complexes highly anisotropic semiconductors, and not any possible (demonstratively negligible) alteration to the effective positive charge on the metal atoms on chain formation.

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(19) Clark, R. J. H.; Dines, T. J. *Chem. Phys. Lett.* **1991**, *185*, 490.