

## Solid-state $^{195}\text{Pt}$ NMR Studies of the Complexes $\text{Pt}(\text{en})\text{Cl}_x$ (en = 1,2-diaminoethane; $x = 2, 3$ or $4$ )

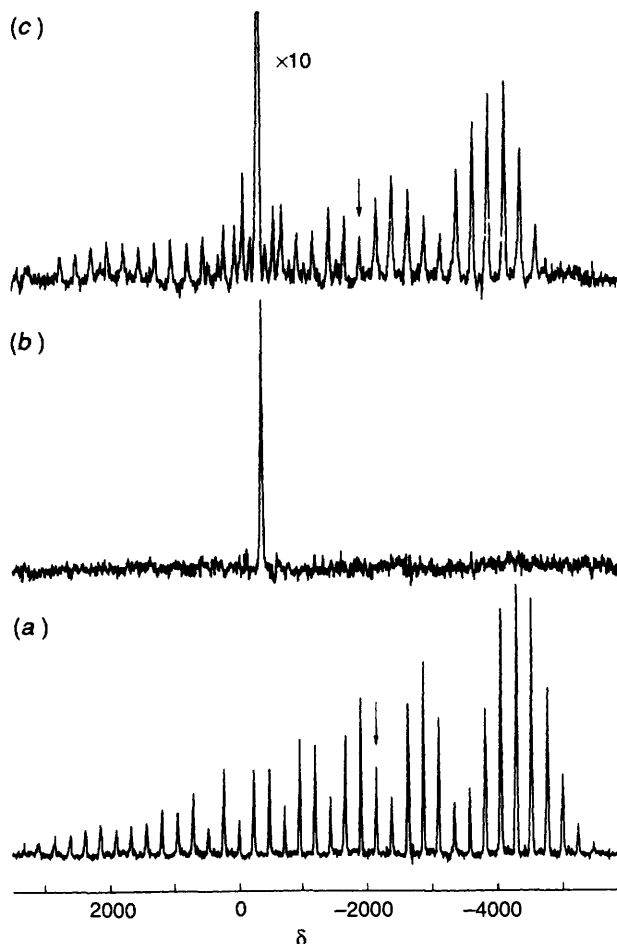
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$^{195}\text{Pt}$  magic-angle spinning (MAS) NMR spectra of the monomeric complexes  $\text{Pt}(\text{en})\text{Cl}_2$  and  $\text{Pt}(\text{en})\text{Cl}_4$  and of the linear-chain complex  $[\text{Pt}(\text{en})\text{Cl}_2][\text{Pt}(\text{en})\text{Cl}_4]$  show that the  $\text{Pt}^{\text{II}}$  and  $\text{Pt}^{\text{IV}}$  sites in the mixed-valence complex have isotropic chemical shifts and shielding anisotropies that are surprisingly similar to those of their monomeric constituents.

There has been interest in mixed-valence linear-chain complexes for many years owing to their unusually anisotropic optical and conductivity properties. In particular the complexes of platinum have been studied widely by a variety of techniques.<sup>1,2</sup> Much of the interpretation of experimental results has been in terms of 'valence delocalization,' with the linear chain being treated as  $\text{Pt}^{2+\alpha}\text{-X-Pt}^{4-\alpha}$  segments, where  $\alpha$  can approach unity. We recently reported  $^{15}\text{N}$  solid-state NMR results on such complexes and found that the  $^{15}\text{N}$  chemical shift and  $J$  coupling to  $^{195}\text{Pt}$  were useful indirect probes of the metal oxidation state.<sup>3</sup> Surprisingly it was found that these parameters, on the formation of the mixed-valence complexes, remained largely unchanged relative to those of the constituent monomeric species. In this paper we explore further the effective oxidation state of the platinum in mixed-valence complexes, but this time more directly using solid-state  $^{195}\text{Pt}$  NMR spectroscopy. This work also demonstrates that it is now possible to obtain good quality  $^{195}\text{Pt}$  MAS NMR spectra of  $\text{Pt}^{\text{II}}$  environments, despite their large chemical shift anisotropy, using the fast spinning speeds that are now commercially available.

There have been numerous useful  $^{195}\text{Pt}$  NMR studies of platinum species in solution.<sup>4</sup> Solid-state NMR spectroscopy has the added advantage that it can provide the principal components of the shielding tensor ( $\sigma_{11}$ ,  $\sigma_{22}$ ,  $\sigma_{33}$ ) as well as the isotropic chemical shift; moreover the spectra are not influenced by solvent or ligand exchange complications. It also has the advantage that it can be applied to materials which are either insoluble or the structures of which are not retained in solution, as is the case for platinum mixed-valence linear-chain complexes. There have, however, thus far been only a few solid-state  $^{195}\text{Pt}$  MAS NMR studies reported in the literature.<sup>5-10</sup> This is principally due to the extremely wide chemical shift range for  $^{195}\text{Pt}$  and the large shielding anisotropies that can occur, particularly for square-planar  $\text{Pt}^{\text{II}}$  sites where anisotropies as large as 10000 ppm have been reported.<sup>6</sup> It is only now that spinning speeds in excess of 12 kHz have become available and hence that MAS studies of such species have become feasible. On the other hand,  $\text{Pt}^{\text{IV}}$  coordination environments are often close to exactly octahedral and so have far smaller shielding anisotropies (up to about 1000 ppm).<sup>5</sup>



**Fig. 1**  $^{195}\text{Pt}$  MAS NMR spectra recorded using a spinning speed of 15.3 kHz: (a)  $\text{Pt}(\text{en})\text{Cl}_2$ , (b)  $\text{Pt}(\text{en})\text{Cl}_4$  and (c)  $[\text{Pt}(\text{en})\text{Cl}_2][\text{Pt}(\text{en})\text{Cl}_4]$ . The  $\text{Pt}^{\text{II}}$  isotropic peak positions are marked by arrows. The spectra were recorded by the ULIRS solid-state NMR facility at University College London on a Bruker MSL-300 spectrometer using a Bruker 4 mm double-bearing probe. High power r.f. pulses of 1  $\mu\text{s}$  were used (equivalent to a 45° flip angle) to ensure reasonably uniform excitation of the wide spectral width under investigation (1 MHz). The baselines have been manually corrected to allow for deadtime effects. The recycle delay between scans was 5 s. High-power decoupling was used during the acquisition time (2 ms). The chemical shift scale is in ppm relative to 1 mol  $\text{l}^{-1}$  aqueous  $\text{Na}_2\text{PtCl}_6$  solution.

$\text{Pt}(\text{en})\text{Cl}_2$  was prepared by a standard route from  $\text{K}_2\text{PtCl}_4$  which was loaned by Johnson Matthey plc.<sup>11</sup>  $\text{Pt}(\text{en})\text{Cl}_4$  was prepared from  $\text{Pt}(\text{en})\text{Cl}_2$  by the chlorine oxidation method of Basolo *et al.*<sup>12</sup> The linear-chain complex was made by the reaction of equimolar amounts of the  $\text{Pt}^{\text{II}}$  and  $\text{Pt}^{\text{IV}}$  monomeric constituents in the presence of hydrochloric acid.

Fig. 1 shows the  $^{195}\text{Pt}$  MAS NMR spectra of  $\text{Pt}(\text{en})\text{Cl}_2$ ,  $\text{Pt}(\text{en})\text{Cl}_4$  and  $[\text{Pt}(\text{en})\text{Cl}_2][\text{Pt}(\text{en})\text{Cl}_4]$  using a spinning speed of 15.3 kHz. Repetition of the experiment using a second spinning speed was sufficient to identify unambiguously the  $\text{Pt}^{\text{II}}$  isotropic resonance, while the spinning sideband manifold provides an indication of the shielding anisotropy. The shielding anisotropy of  $\text{Pt}^{\text{IV}}$  sites was estimated from static NMR spectra which were also recorded on  $\text{Pt}(\text{en})\text{Cl}_4$  and  $[\text{Pt}(\text{en})\text{Cl}_2][\text{Pt}(\text{en})\text{Cl}_4]$ . The results are summarized in Table 1. The isotropic chemical shifts may be compared with those reported for solutions of similar complexes, such as *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_4$  ( $\delta_{\text{iso}} = -145$  in  $\text{H}_2\text{O}$ ) and *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$  ( $\delta_{\text{iso}} = -2048$  to  $-2168$ , depending on solvent).<sup>4</sup>

It is immediately apparent that there is surprisingly little difference between the electronic environments of the  $\text{Pt}^{\text{II}}$  and  $\text{Pt}^{\text{IV}}$  sites in the mixed-valence linear-chain complex compared

**Table 1** Summary of  $^{195}\text{Pt}$  NMR results<sup>a</sup>

Complex	$\text{Pt}^{\text{II}}$			$\text{Pt}^{\text{IV}}$		
	$\delta_{\text{iso}}^b$	$\Delta\sigma^c$	$\eta^c$	$\delta_{\text{iso}}^b$	$\Delta\sigma^c$	$\eta$
$\text{Pt}(\text{en})\text{Cl}_2$	-2154	-8100	0			
$\text{Pt}(\text{en})\text{Cl}_4$				-374	-380	0.14
$[\text{Pt}(\text{en})\text{Cl}_2][\text{Pt}(\text{en})\text{Cl}_4]$	-1924	-7300	0	-328	+230	0.10

<sup>a</sup> Chemical shifts are quoted in ppm relative to 1 mol  $\text{l}^{-1}$  aqueous  $\text{Na}_2\text{PtCl}_6$  solution at 295 K. The anisotropy,  $\Delta\sigma$ , is defined as  $\sigma_{33} - 0.5(\sigma_{11} + \sigma_{22})$ , and the asymmetry parameter,  $\eta$ , by  $(\sigma_{22} - \sigma_{11})/(\sigma_{33} - \sigma_{\text{iso}})$ , where  $\sigma_{\text{iso}} = -\delta_{\text{iso}} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$  and  $|\sigma_{33} - \sigma_{\text{iso}}| > |\sigma_{11} - \sigma_{\text{iso}}| > |\sigma_{22} - \sigma_{\text{iso}}|$ . <sup>b</sup> Values of  $\delta_{\text{iso}}$  are accurate to within  $\pm 8$ . <sup>c</sup> For the  $\text{Pt}^{\text{II}}$  sites, the  $\Delta\sigma$  values were estimated from the fast spinning MAS spectra assuming axial symmetry ( $\eta = 0$ ); the estimated error in  $\Delta\sigma$  is  $\pm 200$ . For the  $\text{Pt}^{\text{IV}}$  sites, the  $\Delta\sigma$  values were obtained from static  $^{195}\text{Pt}$  spectra; the uncertainty in  $\Delta\sigma$  is  $\pm 40$ .

to those in the constituent monomeric species. It is known that  $^{195}\text{Pt}$  chemical shifts are dominated by the paramagnetic shielding contribution, and are particularly sensitive to the number and nature of the ligands bonded to the platinum; they also depend on the platinum oxidation state.<sup>4</sup> Further the shielding anisotropy,  $\Delta\sigma$ , is, in general, a far more sensitive probe of local geometry than is the isotropic chemical shift alone. While  $\Delta\sigma$  for the  $\text{Pt}^{\text{II}}$  site is, as expected, lower for  $[\text{Pt}(\text{en})\text{Cl}_2][\text{Pt}(\text{en})\text{Cl}_4]$  than for  $\text{Pt}(\text{en})\text{Cl}_2$ , the similarity between the values indicates that there is little change in the molecular orbital energy levels of the  $\text{Pt}^{\text{II}}$  site on chain formation. Hence any delocalization of the valence electrons along the chain on formation of the mixed-valence complex must be small.

It is widely accepted that for mixed-valence complexes the valence delocalization increases on changing the halogen from chlorine to bromine to iodine.<sup>1,2</sup> Unfortunately, our attempts to record  $^{195}\text{Pt}$  NMR spectra of the bromide and iodide linear-chain complexes resulted in poor spectra, possibly owing to larger residual direct dipolar coupling between  $^{195}\text{Pt}$  and the halogen in these cases,<sup>13</sup> and also to possible indirect dipolar coupling effects.<sup>9</sup> Isotropic chemical shift positions were successfully identified for  $\text{Pt}(\text{en})\text{I}_2$  ( $\delta_{\text{iso}} = -3288$ ;  $\Delta\sigma = \text{ca. } -6500$ ),  $\text{Pt}(\text{en})\text{I}_4$  ( $\delta_{\text{iso}} = -3605$ ;  $\Delta\sigma = -2180$ ;  $\eta = 0.33$ ) and the  $\text{Pt}^{\text{IV}}$  site in  $[\text{Pt}(\text{en})\text{Br}_2][\text{Pt}(\text{en})\text{Br}_4]$  ( $\delta_{\text{iso}} = -1429$ ).

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