$[Pt\{4,4'-(NO_2)_2\text{-bipy}\}Cl_2]^{2-}$ [4,4′-$(NO_2)_2$-bipy = 4,4′-dinitro-2,2′-bipyridine]: an EPR-active '18 electron' platinum complex

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The complex $[Pt\{4,4'-(NO_2)_2\text{-bipy}\}Cl_2]$ undergoes *four* consecutive one-electron reductions, with a very small $E_1 - E_2$ separation of 180 mV and both the mono- and di-reduction products can be electrochemically generated giving EPR-active solutions: thus $[Pt\{4,4'-(NO_2)_2\text{-bipy}\}Cl_2]$ has a nearly degenerate pair of predominantly ligand-based π^* orbitals.

The unusual redox and photophysical properties of square-planar sixteen-electron Pt^{II} complexes containing α-diimmine ligands is of current interest.[1,2] We have been investigating the complexes of general formula $[Pt(bipy)L_2]^{n+}$ (bipy = 2,2′-bipyridine; L = spectator ligands such as Cl^-).[2] The redox chemistry for the complexes with L = Cl or CN (n = 0), L = NH_3, pyridine or PMe_3 (n = 2) and L_2 = ethylenediamine (n = 2) are all very similar with a reversible one-electron reduction process at *ca.* −1.0 *vs.* Ag/AgCl and a second one-electron quasi-reversible reduction approximately 600 mV more negative. Extensive spectroscopic studies have shown that the LUMO of $[Pt(bipy)L_2]^{n+}$ is primarily bipy π^* based with small but significant (*ca.* 10%) admixtures of Pt 5d and/or 6p orbitals.

We report here the very different electronic behaviour of $[Pt\{4,4'-(NO_2)_2\text{-bipy}\}Cl_2]$. The literature has few examples of complexes of the $(NO_2)_2$-bipy ligand[3] and only one incomplete electrochemical study.[4] The complex is prepared by heating under reflux a suspension of the free ligand in an aqueous solution of $K_2[PtCl_4]$ for 3 h and recrystallisation of the resultant precipitate from hot dmf.§ Cyclic voltammetry in 0.1 M $[NBu^n_4]BF_4$–dmf solution at 298 K reveals four consecutive one-electron reductions at −0.27 (ΔE_{p-p} = 0.080), −0.45 (0.080), −1.05 (0.100) and −1.50 V (0.170 V), respectively, *vs.* Ag/AgCl (Fig. 1).¶ The first two are fully reversible whilst the third and fourth are quasi-reversible and irreversible, respectively.

Electrosynthesis of the formally seventeen-electron species $[Pt\{4,4'-(NO_2)_2\text{-bipy}\}Cl_2]^-$ at −0.37 V and 243 K yields an EPR-active solution. Fluid and frozen-solution X-band spectra (Fig. 2) are similar to those found for $[Pt(bipy)L_2]^{(n-1)+}$ but with smaller hyperfine couplings to ^{195}Pt (34%, I = 1/2).[2] Spectrum simulation[6] yields the spin-Hamiltonian parameters $g_{iso} = 2.006$, $A_{iso(Pt)} = -43 \times 10^{-4}$ cm^{-1} (linewidth $W_{iso} = 12 \times 10^{-4}$ cm^{-1}), $g_1 = 2.039$, $g_2 = 2.012$, $g_3 = 1.972$, $A_{1(Pt)} = -32 \times 10^{-4}$ cm^{-1} ($W_1 = 9 \times 10^{-4}$ cm^{-1}), $A_{2(Pt)} = -48 \times 10^{-4}$ cm^{-1} ($W_2 = 8 \times 10^{-4}$ cm^{-} 1) and $A_{3(Pt)} = -28 \times 10^{-4}$ cm^{-1} ($W_3 = 28 \times 10^{-4}$ cm^{-1}).

Bulk electrogeneration at −0.65 V and 243 K yields the formally eighteen-electron species $[Pt\{4,4'-(NO_2)_2\text{-bipy}\}Cl_2]^{2-}$ which is EPR-active at room temperature and 77 K, indicating that the two reduction electrons are unpaired. The fluid solution spectrum at 293 K exhibits both hyperfine

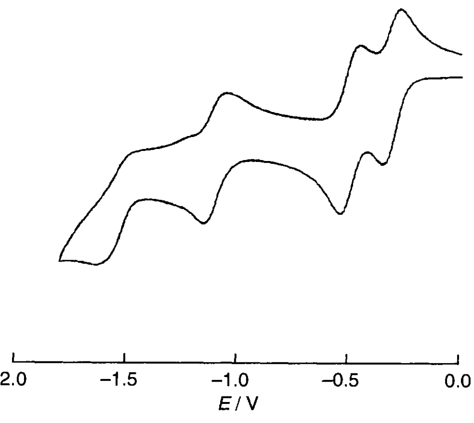

Fig. 1 Cyclic voltammogram of $[Pt\{4,4'-(NO_2)_2\text{-bipy}\}Cl_2]$ in $[NBu^n_4]BF_4$–dmf solutions at 298 K

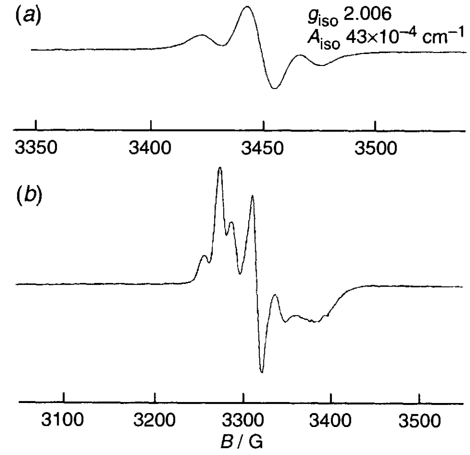

Fig. 2 (*a*) Fluid solution at 298 K, and (*b*) frozen solution at 77 K X-band EPR spectra of $[Pt\{4,4'-(NO_2)_2\text{-bipy})\}Cl_2]^-$ in $[NBu^n_4]BF_4$–dmf

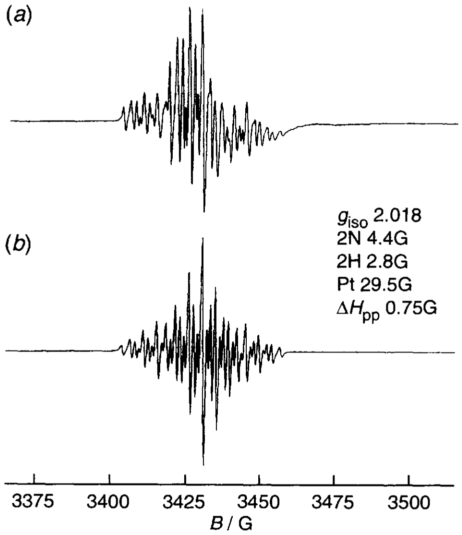

Fig. 3 (*a*) Fluid solution X-band EPR spectrum of $[Pt\{4,4'-(NO_2)_2\text{-bipy}\}Cl_2]^{2-}$ in $[NBu^n_4]BF_4$–dmf at 298 K, and (*b*) simulation using the parameters in the text

Table 1 Nuclear coefficients of LUMO and SLUMO of [Pt{4,4′-$(NO_2)_2$-bipy}Cl_2]

Atom[a]	Orbital[b]	LUMO	SLUMO
$N^{1,1'}$	$2p_z$	0.053	0.031
$C^{2,2'}$	$2p_z$	0.019	0.010
$C^{3,3'}$	$2p_z$	0.014	0.041
$C^{4,4'}$	$2p_z$	0.024	0.015
$C^{5,5'}$	$2p_z$	0.038	0.019
$C^{6,6'}$	$2p_z$	0.018	0.011
$N^{2,2'}$	$2p_z$	0.196	0.228
$O^{1,1'}$	$2p_z$	0.065	0.072
$O^{2,2'}$	$2p_z$	0.065	0.073
Pt	$5d_{yz}$	0.012	—
	$5d_{xz}$	—	0.005
	$6p_z$	0.006	—

[a] $N^{1,1'}$–$C^{6,6'}$ are the ring atoms of the bipy ligand where C^2 and $C^{2'}$ are the bridging C atoms. N^2, $N^{2'}$, O^1, $O^{1'}$, O^2 and $O^{2'}$ refer to the nitro groups. [b] The *z* direction is perpendicular to the plane of the molecule.

coupling to ^{195}Pt and superhyperfine coupling to ligand nuclei, centred at g_{iso} = 2.018 [Fig. 3(*a*)]. This can be simulated by assuming coupling to ^{195}Pt (-27.8×10^{-4} cm^{-1}), to two equivalent ^{14}N nuclei (4.4×10^{-4} cm^{-1}) and to two equivalent ^1H nuclei (2.6×10^{-4} cm^{-1}) with a Lorentzian linewidth of 0.75×10^{-4} cm^{-1} [Fig. 3(*b*)]. We assign the ^{14}N coupling to the nitro-group nitrogens on the basis of extended Hückel molecular orbital (EHMO) calculations (Table 1). Note we do not attempt to assign the positions of the ^1H nuclei. The EHMO calculations suggest that after the N^2 and $N^{2'}$ (the nitro-group nitrogens) superhyperfine coupling the next largest in magnitude should be to N^1 and $N^{1'}$ (the ring nitrogens). However, a better simulation of the experimental spectrum is possible using the model detailed above, *viz.*, coupling to two nitrogen nuclei and two hydrogen nuclei. Thus, the EPR spectra indicate the unpaired electrons to be highly localised on the nitro groups, but clearly there is a significant amount of metal–ligand orbital mixing.

That the direduced complex [Pt{4,4′-$(NO_2)_2$-bipy}Cl_2]$^{2-}$ is EPR-active tells us that the LUMO–second LUMO (SLUMO) gap of [Pt{4,4′-$(NO_2)_2$-bipy}Cl_2] is less than the spin-pairing energy of the two added electrons, consistent with the small $E_1 - E_2$ potential separation of 180 mV. This suggests an almost degenerate pair of low-lying orbitals and EHMO calculations support this model, with a calculated LUMO–SLUMO gap of 200 meV.

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Footnotes

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§ Compound confirmed by single-crystal X-ray structure determination.[5] UV–VIS in dmf solution: MLCT transition at 23 000 cm^{-1} ($\varepsilon = 0.45 \times 10^4$ M^{-1} cm^{-1}).

¶ The ferrocene–ferrocenium couple is measured at +0.55 V on our electrode system. All electrochemical and EPR measurements were recorded as reported previously.[2]

References

1 See, for example: J. A. Zuleta, M. S. Burbery and R. Eisenberg, *Coord. Chem. Rev.*, 1991, **30**, 4446; V. M. Miskowski, V. H., Holding, C.-M. Che and Y. Wang, *Inorg. Chem.*, 1993, **32**, 2518; A. Klein and W. Kaim, *Organometallics.*, 1995, **14**, 1176; S. Hasenzahl, H.-D. Hausen and W. Kaim, *Chem. Eur. J.*, 1995, **1**, 95; A. Klein, W. Kaim, E. Waldhör and H.-D. Hausen, *J. Chem. Soc., Perkin Trans. 2*, 1995, 2121; S. D. Cummings and R. Eisenberg, *J. Am. Chem. Soc.*, 1996, **118**, 1949.

2 D. Collison, E. J. L. McInnes, F. E. Mabbs, K. J. Taylor, A. J. Welch and L. J. Yellowlees, *J. Chem. Soc., Dalton Trans.*, 1996, 329.

3 A. Basu, H. D. Gaffney and T. C. Strekas, *Inorg. Chem.*, 1982, **21**, 2231 and references therein; J. A. Connor, C. Overton and N. E. Murr, *J. Organomet. Chem.*, 1984, **277**, 277; M. J. Cook, A. P. Lewis, G. S. G. McAuliffe, V. Skarda, A. J. Thomson, J. L. Glasper and D. J. Robbins, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1303.

4 L. A. Worf, R. Deusing, P. Chen, L. D. Ciana and T. J. Meyer, *J. Chem. Soc., Dalton Trans.*, 1991, 849.

5 E. J. L. McInnes, L. Rovatti, A. J. Welch and L. J. Yellowlees, in preparation.

6 Anisotropic EPR simulation program for *S* = 1/2, D. Collison and F. E. Mabbs, University of Manchester, England and described in *EPR of d-Transition Metal Compounds*, Elsevier, Amsterdam, 1992, ch. 7; isotropic EPR simulation program, J. M. Rawson, University of Edinburgh, Scotland, 1994.

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