Resonance Raman Spectrum of the Mixed-valence Anion-bridged Complex $Cs_2[Pt(NO_2)(NH_3)Br_2][Pt(NO_2)(NH_3)Br_4]$

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Summary The resonance Raman spectrum of the title complex with 568·2 nm excitation consists of eleven three-or-more-membered progressions, in nine of which the ν_1, $\nu(BrPt^{IV}Br)$, acts as the progression-forming mode, the results yield (among others) $\omega_1 = 179{\cdot}0 \pm 0{\cdot}3\ cm^{-1}$, $x_{11} = -0{\cdot}39 \pm 0{\cdot}04\ cm^{-1}$, and imply a substantial change in the Pt^{IV}–Br chain bond length (along with other structural changes) on excitation of the complex from the ground to the resonant (intervalence) excited state

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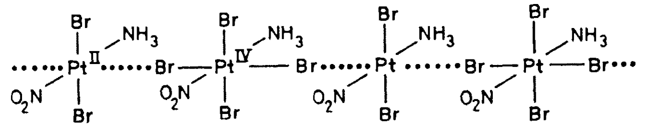
Linear-chain halogen-bridged complexes of platinum are of considerable interest as one-dimensional materials since their electrical conductance ($\sigma_{\|} < 10^{-8}\ \Omega^{-1}\ cm^{-1}$ at 1 atm pressure, but highly pressure dependent) is intermediate between that of insulators such as K_2PtCl_4 and that of conductors such as KCP [$K_2Pt(CN)_4Br_{0\cdot30}\cdot3H_2O$] ($10^2$ Ω^{-1} cm^{-1}).[1,2] They are known to form, with a variety of amines, not only cation chains and neutral chains, but also (in a few cases) anion chains.[3] Resonance Raman (RR) spectra of many types of cation- and neutral-chain complexes are already known to be dominated by long progressions in ν_1, the symmetric X–Pt^{IV}–X stretching mode, of the linear chain[3–5] but the only anion-chain complexes studied so far (partially oxidised Cossa's salt, *etc.*) yielded relatively poor RR spectra.[6] We report herein that the anion-chain complex[7,8] $Cs_2[Pt(NO_2)(NH_3)Br_2][Pt(NO_2)(NH_3)Br_4]$, which is deduced to have the structure (**1**) displays (particularly at *ca.* 80 K) an extremely rich RR spectrum which implies that it not only undergoes a substantial change in the Pt^{IV}–Br bond length in the resonant (intervalence) excited state, but also that there are significant changes along several other co-ordinates.



(1)

Irradiation of the highly dichroic complex (green–gold needles, red powder) with the Kr^+ 568·2 nm line, which falls within the contour of the very intense $Pt^{II} \rightarrow Pt^{IV}$ intervalence transition of the complex centred at 19,000 cm^{-1}, leads to an RR spectrum consisting of eleven progressions of three or more members, in nine of which ν_1 [the $\nu(Br–Pt^{IV}–Br)_s$ axial stretching mode at $\sim 178\ cm^{-1}$] acts as the progression-forming mode. This mode is totally symmetric, as shown by polarised single-crystal studies. The observed progressions (Figure) consist of $v_1\nu_1$ ($v_1 = 1$—7), $v_1\nu_1 + \nu_2$ ($v_1 = 0$—7), $v_1\nu_1 + 2\nu_2$ ($v_1 = 0$—6), $v_1\nu_1 + 3\nu_2$ ($v_1 = 0$—3), $v_1\nu_1 + \delta(NO_2)_s$ ($v_1 = 0$—3), $v_1\nu_1 + \nu(NO_2)_s$ ($v_1 = 0$—3), $v_1\nu_1 + \nu_2 + \delta(NO_2)_s$ ($v_1 = 0$—2), $v_1\nu_1 + 105\cdot9$ ($v_1 = 0$—3), and $v_1\nu_1 + 138\cdot5$ ($v_1 = 0$—3). The enabling modes in the secondary progressions consist of ν_2, the equatorial $BrPt^{IV}Br$ stretching mode (also totally symmetric), $\delta(NO_2)_s$ and $\nu(NO_2)_s$, the symmetric bending and stretching modes of the nitro ligand (833 and 1334 cm^{-1}, respectively), and two unassigned modes at 105·9 and 138·5 cm^{-1}. The remaining two progressions are $v_2\nu_2$ from $v_2 = 1$ to 3 and $v_2\nu_2 + \nu(NO_2)_s$ from $v_2 = 0$ to 2. Many other combination bands are also evident in the RR spectrum. The great detail displayed in this spectrum enables the following harmonic band wavenumbers and anharmonicity constants to be calculated by standard procedures:[9] $\omega_1 = 179\cdot0 \pm 0\cdot3\ cm^{-1}$, $\omega_2 = 207\cdot4 \pm 0\cdot3\ cm^{-1}$, $x_{11} = -\ 0\cdot39 \pm 0\cdot04\ cm^{-1}$, $x_{12} = 0\cdot0 \pm 0\cdot1\ cm^{-1}$, and $x_{22} = -\ 0\cdot25 \pm 0\cdot05\ cm^{-1}$. The principal progression-forming mode, ν_1, is thus close to behaving as a simple harmonic oscillator.

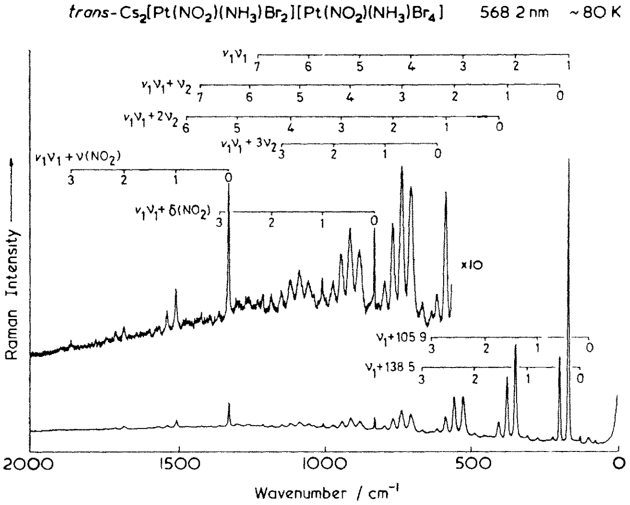


FIGURE. Resonance Raman spectrum of $Cs_2[Pt(NO_2)(NH_3)Br_2]$-$[Pt(NO_2)(NH_3)Br_4]$ at *ca.* 80 K with $\lambda_0 = 568\cdot2$ nm excitation. (Spectral slit width $\sim 1\ cm^{-1}$).

The excitation profiles of ν_1, $2\nu_1$, ν_2, $\nu_1 + \nu_2$ and $\nu(NO_2)_s$ all maximise at *ca.* 17,600 cm^{-1} *i.e.* just on the low energy side of the resonant (intervalence) transition. Although this behaviour of ν_1 and $2\nu_1$ is typical of that of cation-chain and neutral-chain complexes,[3–5] no previously studied chain complexes have bands attributable to modes other than ν_1 and its overtones which have been enhanced at resonance with the inter-valence transition; this implies that there is, for this complex, a significant coupling of the axial mode ν_1 with certain equatorial modes. Indeed, the observation of so many progressions involving both the axial as well as equatorial modes confirms this conclusion. It is of particular interest that the intensities of the symmetric nitro bands, $\delta(NO_2)_s$ and $\nu(NO_2)_s$, as well as that of ν_2, are so affected by the excitation wavelength, implying that the intervalence transition has far-reaching electronic effects on the nature of the equatorial bonds in the complex (although evidently not on the PtN bonds). Possibly this is associated with the π-acceptor character of the nitro group, coupled with the anionic nature of the linear chain (which evidently also leads to low $4f_{7/2}$ and $4f_{9/2}$ Pt binding energies).[8]

The observation of many combination-band progressions of the sort $v_1\nu_1 + v_2\nu_2$ implies that the excited-state potential surface is displaced, with respect to that of the ground state, along both the Q_1 as well as the Q_2 normal co-ordinates, *i.e.* it is possible that the complex exhibits the Duschinsky effect in the inter-valence state.[10,11]

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