Note

Electronic, Raman and Resonance-Raman Spectroscopy of Copper(II)–Platinum(IV) Linear-chain Chloride-bridged Complexes of 1,2-Diaminoethane

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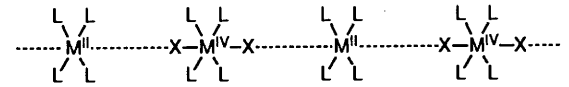
Copper(II)–platinum(IV) linear-chain complexes of the type $[Cu_xPt_{1-x}(en)_2][Pt(en)_2Cl_2][ClO_4]_4$ (en = 1,2-diaminoethane) have been synthesised where $0.58 < x < 1$. The intensely red, highly dichroic needles obtained when $x = 0.58$ become much paler and lose their dichroism as $x \longrightarrow 1$. The intense *z*-polarised band at 18 000–23 000 cm^{-1} (single-crystal transmission) for $x < 1$ is believed to be due to the $Pt^{II} \longrightarrow Pt^{IV}$ intervalence transition of Pt^{II}–Pt^{IV} domains whose symmetric stretching mode ν_1,ν_{sym}(Cl–Pt^{IV}–Cl) occurs at 313 cm^{-1}. For the stoichiometric Cu^{II}–Pt^{IV} chain complex, the $Cu^{II} \longrightarrow Pt^{IV}$ transition probably lies in the ultraviolet region and the ν_1',ν_{sym}(Cl–Pt^{IV}–Cl) stretching mode occurs at 341 cm^{-1}. This band displays no resonance enhancement with any excitation lines in the visible or near-ultraviolet region; both this fact, as well as the high value for ν_1', imply that the stoichiometric material is highly valence localised, as expected for a system consisting of chains in which the unpaired electrons are in $d_{x^2-y^2}$ orbitals (*i.e.*, ⊥ chain direction) on metal ions which are 10.8 Å apart.

Large numbers of halide-bridged mixed-valence complexes of nickel, palladium and platinum analogous to Wolffram's red salt, $[Pt(NH_2Et)_4][Pt(NH_2Et)_4Cl_2]Cl_4{\cdot}4H_2O$, have now been synthesised.[1] These are all linear-chain complexes of the general type shown below, where M = Pt, Pd or Ni, X = Cl, Br or I,



and L = equatorial ligand. The structure of such complexes varies from highly localised-valence species in which the M^{IV}–X/M^{II}–X distance ratio is *ca.* 0.75 to fully delocalised nickel(III) chain complexes in which it is unity.[2] The electrical conductivity of such complexes along the chain covers the enormous range of 10^{-15}–1 Ω^{-1} cm^{-1}, being least for the most Peierls-distorted species.[3] In this context, the most localised valence of such species are the mixed-metal ones, Pd^{II}–Pt^{IV} [4] and Ni^{II}–Pt^{IV},[5–7] as judged by the high wavenumbers for both their intervalence transitions and their ν_1',ν_{sym}(X–Pt^{IV}–X) symmetric stretching modes. A recent report of a non-stoichiometric $Cu_{0.89}$–$Pt_{1.11}$ linear-chain complex,[8,*] isomorphous with the well known Pt^{II}–Pt^{IV} complex $[Pt(en)_2][Pt(en)_2Cl_2][ClO_4]_4$ (en = 1,2-diaminoethane), is of interest as a new material with unique properties; however, some features of its reported properties seemed at odds with our own expectations. We now report the results of a study of such materials over the range $0.58 < x < 1$ which reveal that some of the key spectroscopic features require reinterpretation. The present report concentrates on the electronic, Raman and resonance-Raman spectra of chloride-bridged complexes belonging to this family of materials, results which make clear that the stoichiometric Cu^{II}–Pt^{IV} compound has highly localised valences and a ν_1' band which is not resonance enhanced with any excitation line in either the visible or near-ultraviolet region.

Experimental

Synthesis.—The monomeric species $[Cu(en)_2Cl_2]$ and $[Pt(en)_2Cl_4]$ were prepared by standard routes.[9,10] They were then mixed in aqueous solution in stoichiometric quantities under various conditions of temperature, concentration, excess of $[ClO_4]^-$ counter anion, and dried to obtain crystals of different Cu:Pt ratios, the aim being to obtain a ratio of 1:1. The ratio was determined from the copper content by atomic absorption measurements. Microanalysis yielded, for example, for the sample with $x = 0.99$ (Found: C, 10.1; H, 3.30; Cl, 22.2_5; N, 11.4. Calc. for $C_8H_{32}Cl_6Cu_{0.99}N_8O_{16}Pt_{1.01}$: C, 9.90; H, 3.35; Cl, 21.9_5; N, 11.5_5%).

Copper percentages and calculated Cu:Pt ratios are listed in Table 1. One powder sample was prepared by rapid precipitation in a large excess of perchlorate as counter anion. Owing to perchlorate impurity, a useful copper analysis could not be carried out on this sample but it is believed to have a Cu:Pt ratio very close to unity. Analogous bromide derivatives could be prepared similarly.

Spectroscopy.—The electronic spectra were recorded for single crystals and pressed discs of the complexes (NaCl:complex = 100:1) by transmission on a Varian 2390 spectrometer at 295 K over the range 350–800 nm. Raman and resonance-Raman spectra were recorded on samples at *ca.* 80 K on a modified Spex 1401 spectrometer with f/1.2 collection optics (Yashica) and on a Spex 14018 spectrometer, excitation being from Coherent models CR18, CR52, CR3000K and Innova 70 lasers. Samples were in the form of pressed discs, either of the pure complex or of the complex dispersed in $KClO_4$. The discs were held at 50–80 K using a cryostat. Calibration was made by reference to the Rayleigh line and also to suitable plasma lines. Infrared spectra were recorded on a Perkin-Elmer 337 spectrometer at 295 K over the range 180–4000 cm^{-1}.

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[*] The M^{IV}–Cl and M^{II}–Cl distances in the Cu^{II}–Pt^{IV} complex (2.318 and 3.085 Å, respectively) are nearly identical with the corresponding ones in the analogous Pt^{II}–Pt^{IV} complex (2.313 and 3.081 Å, respectively).

Table 1 Summary of spectroscopic results for the copper–platinum complexes

Sample[a]	%Cu	Colour	λ_{max}/nm	λ_0/nm	ν_1'(Cu–Pt)/ cm^{-1}	ν_1(Pt–Pt)/ cm^{-1}	$I(\nu_1')/I(\nu_1)$
(*a*) $[Cu_{0.58}Pt_{0.42}(en)_2][Pt(en)_2Cl_2][ClO_4]_4$	3.79	Red	420[b] 490[c]	676.4	340	309	0.003
(*b*) $[Cu_{0.97}Pt_{0.03}(en)_2][Pt(en)_2Cl_2][ClO_4]_4$	6.36	Red	420[b]	676.4	341	322.5	0.99[d]
(*c*) $[Cu_{0.97}Pt_{0.03}(en)_2][Pt(en)_2Cl_2][ClO_4]_4$	6.39	Red	420[b]	676.4	340	322	0.99[d]
$[Cu_{0.99}Pt_{0.01}(en)_2][Pt(en)_2Cl_2][ClO_4]_4$	6.48	Red	420[b]	676.4	340	322	2.26[d]
(*d*) $[Cu(en)_2][Pt(en)_2Cl_2][ClO_4]_4$	*e*	Red	420[b]	676.4	342	321	13.9[f]

[a] Samples (*a*)–(*d*) refer to Figs. 2 and 3. [b] Transmission by pressed disc with NaCl matrix. [c] Single-crystal transmission. [d] Scattering from single crystal. [e] Preparation was by fast precipitation in the presence of an excess of perchlorate, %Cu could therefore not be determined (see text); however the properties of the complex indicate that the Cu : Pt ratio is 1.00 (%Cu = 6.57). [f] Scattering from pressed disc.

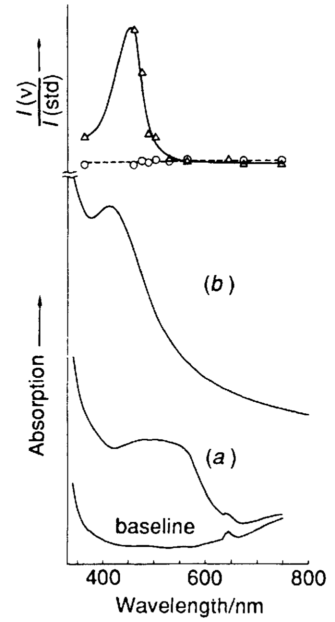

Fig. 1 Transmission electronic spectra of $[Cu_xPt_{1-x}(en)_2][Pt(en)_2Cl_2][ClO_4]_4$ [baseline refers only to spectrum (*a*)] for $x = 0.58$ (single crystal) (*a*) and $x = 0.97$ (pressed NaCl disc) (*b*), together with the excitation profiles of the ν_1 and ν_1' bands at 322 (△, Pt^{II}–Pt^{IV} domains) and 340 cm^{-1} (○, Cu^{II}–Pt^{IV} domains), respectively, from a sample containing 6.36% Cu ($x = 0.97$)

Results and Discussion

Electronic spectra are shown in Fig. 1 and some of the Raman and resonance-Raman spectra in Figs. 2 and 3; the results are summarised in Table 1. Raman band wavenumbers and assignments for a representative spectrum are given in Table 2. Red crystals with a copper percentage of 6.36% (corresponding to a Cu : Pt ratio of 0.97 : 1.03), *i.e.* approaching closely to the theoretical value of 6.57% for a Cu : Pt ratio of 1, were found to be scarcely dichroic, with an electronic band maximum (pressed disc) at around 420 nm (sample independent). Raman spectra of a single crystal from the same preparation (Figs. 2 and 3) show a number of bands at low wavenumbers not observed for the discrete copper(II) and platinum(IV) constituent complexes. With an excitation wavelength of 676.4 nm, Raman bands at 322 and 341 cm^{-1} occur with approximately equal intensity. On changing to $\lambda_0 = 514.5$ nm, the 322 cm^{-1} band is greatly enhanced, showing a weak overtone progression, whereas the 341 cm^{-1} band is not.

Other samples containing greater than 6% copper gave similar results. It seems likely[11] that the red-brown colour possessed by these crystals arises principally from the $d_{xy} \longrightarrow d_{x^2-y^2}$ transition within localised Cu^{II} units and, to a slight extent, from the intervalence charge-transfer (i.v.c.t.) absorption of Pt^{II}–Pt^{IV} domains or chain sections.

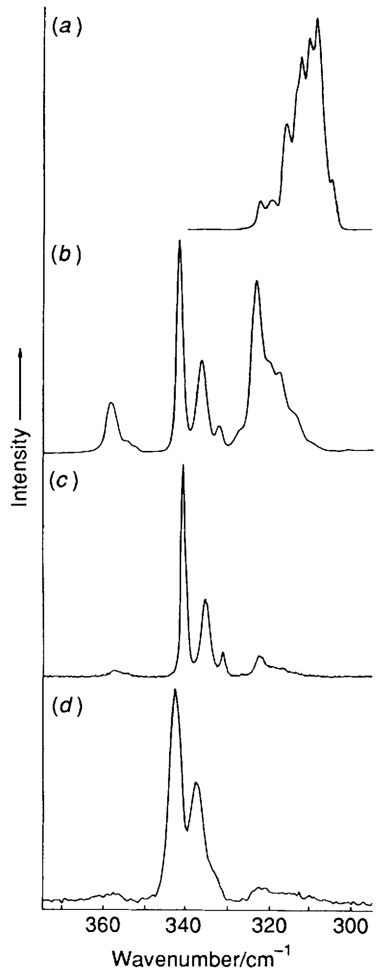

Fig. 2 The 295–375 cm^{-1} region of Raman and resonance-Raman spectra, taken at 80 K, of $[Cu_xPt_{1-x}(en)_2][Pt(en)_2Cl_2][ClO_4]_4$; λ_0 = 676.4 nm, slitwidth = 200 µm. For sample identification, see Table 1

On going to crystals containing a smaller copper percentage the crystals become more intensely coloured and dichroic and the Raman band at 322 cm^{-1} becomes more intense than that at 341 cm^{-1}. Thus, in the case of a crystal with 3.79% copper (corresponding to a Cu : Pt ratio of 0.58 : 1.42), the single-crystal transmission electronic spectrum shows a strong absorption band centred at 490 nm. This band is almost certainly due to charge transfer between Pt^{II} and Pt^{IV}, the i.v.c.t. band maximum having previously been reported to occur at 500 nm for the stoichiometric Pt^{II}–Pt^{IV} complex.[12] In the Raman/resonance-Raman spectrum the ν_1 band at smaller shift, then occurring at 309 cm^{-1}, is observed to extend to $v_1 = 16$ with $\lambda_0 = 514.5$ nm. Thus the relative intensities of the bands ν_1 and ν_1' may be correlated approximately with the percentage of copper present, *i.e.* with the Cu : Pt ratio. Excitation profiles were determined for both bands, with excitation wavelengths throughout the visible

Table 2 Wavenumbers, $\tilde{\nu}$, relative intensities, $I(\tilde{\nu})/I(\nu_1)$, full widths at half maximum, $\Delta\tilde{\nu}_{\frac{1}{2}}$ and assignments of bands in the Raman spectrum of $[Cu_{0.97}Pt_{0.03}(en)_2][Pt(en)_2Cl_2][ClO_4]_4$*

$\tilde{\nu}$/cm^{-1}	$I(\tilde{\nu})/I(\nu_1)$	$\Delta\nu_{\frac{1}{2}}$/cm^{-1}	Assignment
188	0.09	14	
291	0.04	6	ν_a
312	0.38	9.5	$\nu_1,\nu_{sym}(^{37}Cl-Pt-^{37}Cl)$
316.5	0.67	9.5	$\nu_1,\nu_{sym}(^{37}Cl-Pt-^{35}Cl)$
321.5	1.00	9.5	$\nu_1,\nu_{sym}(^{35}Cl-Pt-^{35}Cl)$
331	0.09	3.0	$\nu_1',\nu_{sym}(^{37}Cl-Pt-^{37}Cl)$
336	0.29	3.8	$\nu_1',\nu_{sym}(^{37}Cl-Pt-^{35}Cl)$
341	0.47	3.8	$\nu_1',\nu_{sym}(^{35}Cl-Pt-^{35}Cl)$
357.5	0.39	4.8	$\nu_2,\nu_{asym}(Cl-Pt-Cl)$
521	0.03	3.2	
582	0.03	4.4	$2\nu_a$
622	0.04	6	$\nu_a + \nu_1',\nu_{sym}(^{37}Cl-Pt-^{35}Cl)$
630.5	0.05	6	$\nu_a + \nu_1',\nu_{sym}(^{35}Cl-Pt-^{35}Cl)$
640	0.04	12	$2\nu_1,\nu_{sym}(^{35}Cl-Pt-^{35}Cl)$
671	0.03	6	$2\nu_1',\nu_{sym}(^{37}Cl-Pt-^{35}Cl)$
677	0.03	6	$2\nu_1',\nu_{sym}(^{35}Cl-Pt-^{35}Cl)$
889.5	<0.01	4	
927	0.02	6	
935	0.03	6	

* λ_0 = 514.5 nm; $\nu_1' = \nu_{sym}(Cl-Pt^{IV}-Cl)$ for the stoichiometric $Cu^{II}-Pt^{IV}$ chain; $\nu_1 = \nu_{sym}(Cl-Pt^{IV}-Cl)$ for the $Pt^{II}-Pt^{IV}$ domains in the chains; ν_a is an unassigned enabling mode.

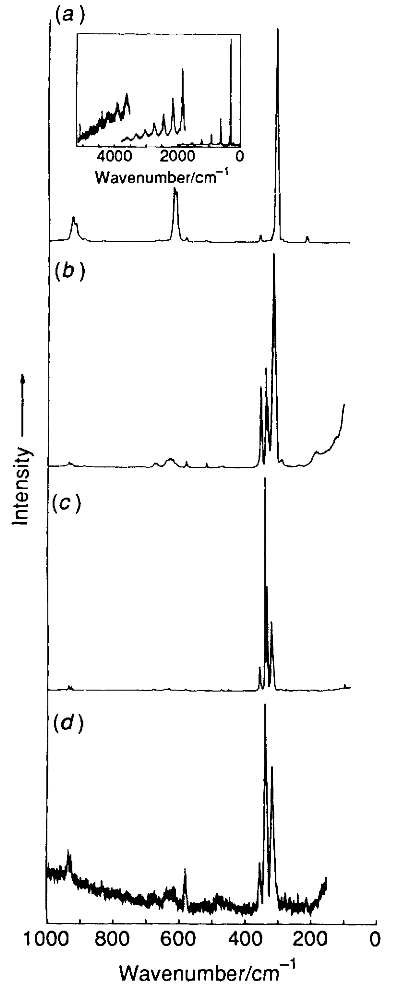

Fig. 3 Raman and resonance-Raman spectra, taken at 80 K, of $[Cu_xPt_{1-x}(en)_2][Pt(en)_2Cl_2][ClO_4]_4$; λ_0 = 514.5 nm, slitwidth = 200 µm. For sample identification, see Table 1

region (Fig. 1), for a sample with a Cu:Pt ratio of 0.97:1.03. There is no significant enhancement of the 341 cm^{-1} band throughout the visible region, but the profile of the 322 cm^{-1} band indicates a strong enhancement maximising at approximately 22 000 cm^{-1}.

It seem likely that the band at 322 cm^{-1} should be assigned to ν_1, the $\nu_{sym}(Cl-Pt^{IV}-Cl)$ symmetric stretching mode, either from domains of $Pt^{II}-Pt^{IV}$ chains in $Cu^{II}-Pt^{IV}$ chains or from chains exclusively of $Pt^{II}-Pt^{IV}$ impurity interspersed among $Cu^{II}-Pt^{IV}$ chains. Most probably, domains of all-platinum chains occur along the copper–platinum chains. This would account for both the variation in wavenumbers of the ν_1 band at smaller Raman shift with copper content (as the Pt^{II} content increases at the expense of the Cu^{II} content, so the ν_1 band wavenumber approaches that for the all $Pt^{II}-Pt^{IV}$ case) as well as for the observed enhancement of the ν_1 band, which differs somewhat from that observed in the all $Pt^{II}-Pt^{IV}$ case;[12] for the latter the maximum in the excitation profile occurs at 17 000 cm^{-1} rather than 22 000 cm^{-1}. The band at 341 cm^{-1} may be assigned to the ν_1' symmetric stretch, $\nu_{sym}(Cl-Pt^{IV}-Cl)$, of the $Cu^{II}-Pt^{IV}$ chain. The higher wavenumber of ν_1' compared with ν_1 in the $Pt^{II}-Pt^{IV}$ chain or in the $Ni^{II}-Pt^{IV}$ (325 cm^{-1})[4] or $Pd^{II}-Pt^{IV}$ (328 cm^{-1}) cases[3] is due to lesser valence delocalisation between the metal atom sites in the $Cu^{II}-Pt^{IV}$ complex, *i.e.* the platinum is closer to oxidation state +4 in the Cu–Pt complex than in the other analogues mentioned above. Nevertheless, ν_1' is some 6 cm^{-1} lower than ν_1 of the discrete complex *trans*-$[Pt(en)_2Cl_4]$, for which it occurs at 347 cm^{-1}, indicating significant (albeit small) interaction between the Cu and Pt units. The absence of strong colour or dichroism in this complex suggests that little or no intervalence charge transfer occurs and that there is probably little or no electron–phonon interaction. This is borne out by the absence of enhancement to the ν_1' band, using either visible or near-ultraviolet excitation.

It is noteworthy that the ν_1 band of the $Pt^{II}-Pt^{IV}$ sections shows considerable structure [up to eight components being observable, Fig. 3(*a*)], while the ν_1' band of the $Cu^{II}-Pt^{IV}$ complex shows just an approximate 9:6:1 triplet, in accordance with expectation for an uncoupled $\nu_{sym}(Cl-Pt^{IV}-Cl)$ symmetric stretching vibration.[13] The complicated structure to the ν_1 band has been observed in numerous cases and is not yet fully explained. However, it is observed only in cases of strong electron–phonon interaction; its absence from the Raman spectrum of the $Cu^{II}-Pt^{IV}$ complex is further evidence for the absence of such coupling in this complex.

Neither the 322 nor the 341 cm^{-1} Raman-active modes give rise to infrared bands, consistent with their assignments to symmetric modes in which there is no detectable change to the dipole moment during the vibration. The asymmetric $Cl-Pt^{IV}-Cl$ stretch occurs at 354 cm^{-1} in these salts, and ν(Pt–N) at 527 cm^{-1}.

The assignment by Oshio *et al.*[8] for the $Cu^{II}-Pt^{IV}$ complex with $x = 0.89$ of an intense, *z*-polarised, electronic band at 22 000 cm^{-1} to the i.v.c.t. transition from Cu^{II} to Pt^{IV} is believed to be incorrect. As outlined above, it seems more likely that this band should be attributed to $Pt^{II} \longrightarrow Pt^{IV}$ transitions of $Pt^{II}-Pt^{IV}$ domains in the chains. The assignment of a strongly enhanced Raman band at 313 cm^{-1} (λ_0 = 514.5 nm) to $\nu_1'(Cl-Pt^{IV}-Cl)$ of the $Cu^{II}-Pt^{IV}$ chain is also believed to be erroneous, the band being best attributed to $\nu_1,\nu_{sym}(Cl-Pt^{IV}-Cl)$ of $Pt^{II}-Pt^{IV}$ domains in the chains. In the Raman spectrum of Oshio *et al.*[8] the unenhanced ν_1' band of $[Cu(en)_2][Pt(en)_2Cl_2][ClO_4]_4$ at approximately 340 cm^{-1} was masked by the much more intense ν_1 band progression of $[Pt(en)_2][Pt(en)_2Cl_2][ClO_4]_4$ arising from the presence of substantial amounts of that complex.

Analogous bromide-bridged complexes can likewise be prepared; these differ widely in appearance, from lustrous green and dichroic (purple as a powder) for the complex with 0.83% copper to red-brown and non-dichroic (orange powder, λ_{max} *ca.* 420 nm) for that with *ca.* 6% copper, *i.e.* effectively for the $Cu^{II}-Pt^{IV}$ complex. The electronic spectral properties thus vary, as for the chloride-bridged analogues, from those characteristic of the pure Pt^{II}–Pt^{IV} complex to those more typical of a Cu^{II} ligand-field transition rather than an i.v.c.t. transition. Nevertheless the Raman spectra of the bromide-bridged species always appear to be dominated by the bands attributed to the $\nu_1,\nu_{sym}(Br–Pt^{IV}–Br)$, fundamental (171–174 cm^{-1}) and its overtones (to $v_1 = 7$ with $\lambda_0 = 676.4$ nm). Such bands probably arise from some Pt^{II}–Pt^{IV} domains within the chains of all the complexes studied, bands which (through resonance effects) mask any arising from ν_1'.

In conclusion, $[Cu(en)_2][Pt(en)_2Cl_2][ClO_4]_4$ appears to be a typical class I, or highly localised valence complex, in which the d^9 Cu^{II} ions act as insulating units along the chain.

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