

NYHOLM LECTURE*

Synthesis, Structure, and Spectroscopy of Metal–Metal Dimers, Linear Chains, and Dimer Chains

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1 Introduction

This lectureship, founded in 1973 to commemorate the name of Sir Ronald Nyholm, is intended in alternate years to be concerned with subjects of interest to inorganic chemists and to have regard for his wide international interests. Little restriction is imposed by the former condition; nor, for an antipodean with a penchant for travel, does the latter. Early studies at Canterbury University College of the University of New Zealand with W. S. Metcalf on diffusion controlled reactions, at the University of Otago with W. S. Fyfe on the effects of pressure on the electrical conductivity of weak electrolytes, and at University College London with Ron Nyholm on the chemistry of the early transition elements, led to my own research interests having a very wide and international base. Complete changes of research area early in one's career, disruptive as they are in the narrowest sense, nevertheless are an enriching experience, the potential benefits of which are too often overlooked by graduates in the UK today.

Ron Nyholm is remembered with warmth and real affection by all who knew him,¹ and he is also remembered for several of his classic statements regarding inorganic chemistry. His definition of the subject, delivered in his inaugural lecture at University College London on 1 March 1956,² was as follows:

'The integrated study of the formation, composition, structure, and reactions of the chemical elements and their compounds, excepting most of those of carbon.'

Over a sherry or two, the word 'most' would readily become displaced by 'some'. He was also perceptive in recognizing the paramount need for equipping Chemistry Departments with all relevant apparatus if they were to carry out first-class research. To quote:²

'Without this costly capital investment in research equipment, university departments must be prepared to limit their objectives to relatively neglected fields away from the broad front of modern scientific advancement and to forfeit

* Delivered at the Nyholm Symposium, University College London, on 6 December 1989, and on other occasions at Lancaster, Bristol, Christchurch, Wellington, Dundee, Manchester, and Glasgow.

¹ D. P. Craig, *Biographical Memoirs of Fellows of the Royal Society*, 1972, 445.

² R. S. Nyholm, Inaugural Lecture, 'The Renaissance of Inorganic Chemistry', University College London, 1 March 1956.

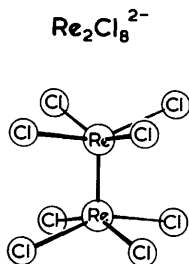


Figure 1 The structure of the $[\text{Re}_2\text{Cl}_8]^{2-}$ ion

their place at the frontiers of knowledge to those with the necessary instruments of attack.'

These comments remain as true today as they were when first made in 1956. Ron Nyholm was responsible for initiating the systematic exploitation of a range of methods for the study of structure and properties of inorganic compounds. But his contribution to the subject was greater than implied by this comment alone. Joseph Chatt summed the situation up well when, in his Memorial Lecture of 1972, he said:³

'It was the infectious enthusiasm and forceful lecturing of Nyholm which prompted the renaissance of Inorganic Chemistry in the UK during the 1950's.'

According to my own observations, the only matters to which Ron Nyholm took exception were those to do with (a) people who spilled *o*-phenylene-bisdimethylarsine, the immensely versatile chelating ligand with which he made his name and which, in 1958, took three months to synthesize (b) late arrival of research students in the laboratory (c) derogatory references to Australia, and (d) students making a mockery of examinations.

One of Ron Nyholm's greatest interests in 1971 was the topic of metal–metal bonding and, accordingly, I have based the Nyholm lecture on or around this topic. His interest began, in association with Jack Fergusson, with the synthesis of the red complex CsReCl_4 .^{4,5} On account of its diamagnetism it was initially thought that this complex might prove to contain the first example of a spin-paired (e^4) tetrahedral ion. Although this did not prove to be the case, nevertheless the complex was found in 1963 to be a trimer $\text{Cs}_3[\text{Re}_3\text{Cl}_{12}]$ possessing an extremely interesting structure. The triangle of rhenium atoms is the key feature in which three rhenium–rhenium bonds of bond order two are implicit.^{5–7}

Shortly after the discovery of this complex another substance with the same empirical formula was isolated as blue crystals. This proved to be $\text{Cs}_2[\text{Re}_2\text{Cl}_8]$, a

³ J. Chatt, Plenary Lecture, 'Ronald Sydney Nyholm', International Conference on Coordination Chemistry, Toronto, 1972

⁴ J. Fergusson, PhD thesis, University of London 1960

⁵ W. T. Robinson, J. E. Fergusson, and B. R. Penfold, *Proc. Chem. Soc.*, 1963, 116

⁶ J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *J. Am. Chem. Soc.*, 1963, **85**, 1349

⁷ J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *Inorg. Chem.*, 1963, **2**, 1166

complex involving the highly symmetric (D_{4h}) anion $[\text{Re}_2\text{Cl}_8]^{2-}$ (Figure 1).^{8,9} Although I was not at this stage directly involved, research in this area was clearly a matter of great general interest. The recognition that ions of this sort must be held together by rhenium–rhenium bonds alone (formally quadruple) prompted many further studies and developments in the chemistry of metal–metal bonded complexes.¹⁰ It was not until the early 1970's that I took a direct interest in metal–metal bonded complexes, and that came about through the realization that they were ideal subjects for electronic, infrared, Raman, and, in particular, resonance Raman studies.^{11,12} Such knowledge was clearly of critical importance to the understanding of the electronic and vibrational spectra of the ions and thus for the proper understanding of the bonding. In these contexts, the $[\text{M}_2\text{X}_8]^{n-}$ ions were of pivotal importance. Subsequently, important questions arose in the spectroscopy of the analogous $\text{M}_2(\text{carboxylate})_4$ complexes. Both subjects are addressed in this lecture, which is then developed into the areas of linear-chain and dimer-chain chemistry, structure, and spectroscopy.

2 Metal–Metal Bonded Complexes

A. Spectroscopy of $[\text{M}_2\text{X}_8]^{n-}$ Ions.—The general philosophy of the research on metal–metal bonded complexes at University College London in the 1970's revolved around the realization that it was essential to be able to assign the electronic and vibrational spectra of structurally and chemically simple metal–metal bonded complexes before it was worthwhile paying attention to these matters for more complicated metal–metal bonded complexes.

With this in mind, it was important to demonstrate that very intense RR spectra of the $[\text{Mo}_2\text{Cl}_8]^{4-}$, $[\text{Mo}_2\text{Br}_8]^{4-}$, $[\text{Re}_2\text{Cl}_8]^{2-}$, and $[\text{Re}_2\text{Br}_8]^{2-}$ ions could be obtained at resonance with the lowest electronic bands of these ions.^{13–15} Such spectra (*A*-term RR spectra)¹² took the form of long progressions in the ν_1 mode, the ReRe stretching mode, implying (a) that the resonant electronic transition is electric dipole allowed and (b) that on transition from the ground to this excited state the ions suffer a substantial change to the metal–metal bond length. These results allowed the resonant electronic transition to be assigned to the ${}^1A_{2u} \leftarrow {}^1A_{1g}, \delta^* \leftarrow \delta$ transition since, on excitation to the δ^* state, the metal–metal bond order would be reduced from four to three with consequential elongation of the metal–metal bond.

Some years later it proved possible to elaborate on these studies in a very effective way. First, the synthesis of the remaining two ions $[\text{Re}_2\text{F}_8]^{2-}$ and $[\text{Re}_2\text{I}_8]^{2-}$ of the set of four structurally similar $[\text{Re}_2\text{X}_8]^{2-}$ ions was

⁸ F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, 1965, **4**, 326.

⁹ F. A. Cotton and C. B. Harris, *Inorg. Chem.*, 1965, **4**, 330.

¹⁰ F. A. Cotton and R. A. Walton, 'Multiple Bonds between Metal Atoms', Wiley, New York, 1982.

¹¹ R. J. H. Clark in 'Advances in Infrared and Raman Spectroscopy', Heyden, London, 1975, p. 143.

¹² R. J. H. Clark and T. J. Dines, *Angew. Chem., Int. Ed.*, 1986, **25**, 131.

¹³ R. J. H. Clark and M. L. Franks, *J. Am. Chem. Soc.*, 1975, **97**, 2691.

¹⁴ R. J. H. Clark and M. L. Franks, *J. Am. Chem. Soc.*, 1976, **98**, 2763.

¹⁵ R. J. H. Clark and N. R. D'Urso, *J. Am. Chem. Soc.*, 1978, **100**, 3088.

accomplished.^{16–18} Second, the development of new lasing dyes in the blue (stilbene 1 and 3) and red (LD 700) together with the availability of UV lines (Ar^{2+} , Kr^{2+}) permitted relatively easy coverage of the wide excitation range of 330–800 nm. Thus it became possible to excite within the contour of each electronic band of each ion; in this way the nature of each excited state of each ion could be probed.

Resonance Raman spectra of each ion, taken at resonance with the electronic band of lowest wavenumber in each case (Figure 2), display long progressions (Figure 3) in ν_1 , the symmetric ReRe stretching mode (318, 275, 276, and 257 cm^{-1} for X = F, Cl, Br, and I, respectively). This clearly indicates the similar nature of the lowest electronic transition of each ion and, by comparison with the earlier work, the assignment of the lowest band to the $\delta^* \leftarrow \delta$, ${}^1A_{2u} \leftarrow {}^1A_{1g}$ transition. This conclusion is substantiated by the observation that the depolarization ratio of the ν_1 bands of $[\text{Re}_2\text{F}_8]^{2-}$, $[\text{Re}_2\text{Cl}_8]^{2-}$ and $[\text{Re}_2\text{Br}_8]^{2-}$ are all $\frac{1}{2}$ at resonance, a situation which can only obtain if the resonant electronic transition is z-polarized (consistent with its assignment to a ${}^1A_{2u} \leftarrow {}^1A_{1g}$ transition in the point group D_{4h}).

Irradiation within the contour of the second electronic transition of each ion produces entirely different RR spectra in each case. These spectra (Figure 4) are characterized by resonance enhancement to bands attributed to the ν_2 mode and its overtones, where ν_2 is the totally symmetric metal–halogen stretching mode (624, 362, 211, and 152 cm^{-1} for X = F, Cl, Br, and I, respectively). Thus the principal structural change undergone by each ion on excitation is, in this case, along the metal–halogen coordinate, a result in keeping with that expected in consequence of a non-bonding-to-antibonding halogen-to-metal charge-transfer transition. The assignment of the second strong band in the electronic spectra of the $[\text{Re}_2\text{X}_8]^{2-}$ ions to the $b_{1u}(\delta^*) \leftarrow (X)e_g(\pi)$, ${}^1E_u \leftarrow {}^1A_{1g}$, transition follows naturally. This assignment is confirmed by the fact that the measured depolarization ratio of the ν_2 band of the $[\text{Re}_2\text{Cl}_8]^{2-}$ and $[\text{Re}_2\text{Br}_8]^{2-}$ ions at resonance is $\frac{1}{8}$, a situation which can only obtain if the resonant electronic transition is xy polarized. This is precisely the polarization required (in D_{4h}) for the ${}^1E_u \leftarrow {}^1A_{1g}$ transition.

RR spectra obtained at resonance with the third electronic band of each ion lead to resonance enhancement to both the ν_1 and ν_2 bands (and their overtones) to comparable extents. Although no firm assignment of the resonant electronic band can be made in this case, the results are consistent with the assignment $e_g(\pi^*) \leftarrow e_u(\pi)$. This transition has been shown, by X α SCF calculations^{19–21} to be between metal-based orbitals with a considerable amount

¹⁶ W. Preetz and L. Rudzik, *Angew. Chem.*, 1979, **91**, 159.

¹⁷ W. Preetz, G. Peters, and L. Rudzik, *Z. Naturforsch., Teil B*, 1979, **34**, 1240.

¹⁸ H. D. Glicksman and R. A. Walton, *Inorg. Chem.*, 1978, **17**, 3197.

¹⁹ A. P. Mortola, J. W. Moskowitz, N. Rösch, C. D. Cowman, and H. B. Gray, *Chem. Phys. Letters*, 1975, **32**, 283.

²⁰ F. A. Cotton, *J. Mol. Struct.*, 1980, **59**, 97.

²¹ R. J. H. Clark and M. J. Stead, in 'Inorganic Chemistry Towards the 21st Century', ACS Symposium Series, No. 211 ed. M. H. Chisholm, 1983, p. 235.

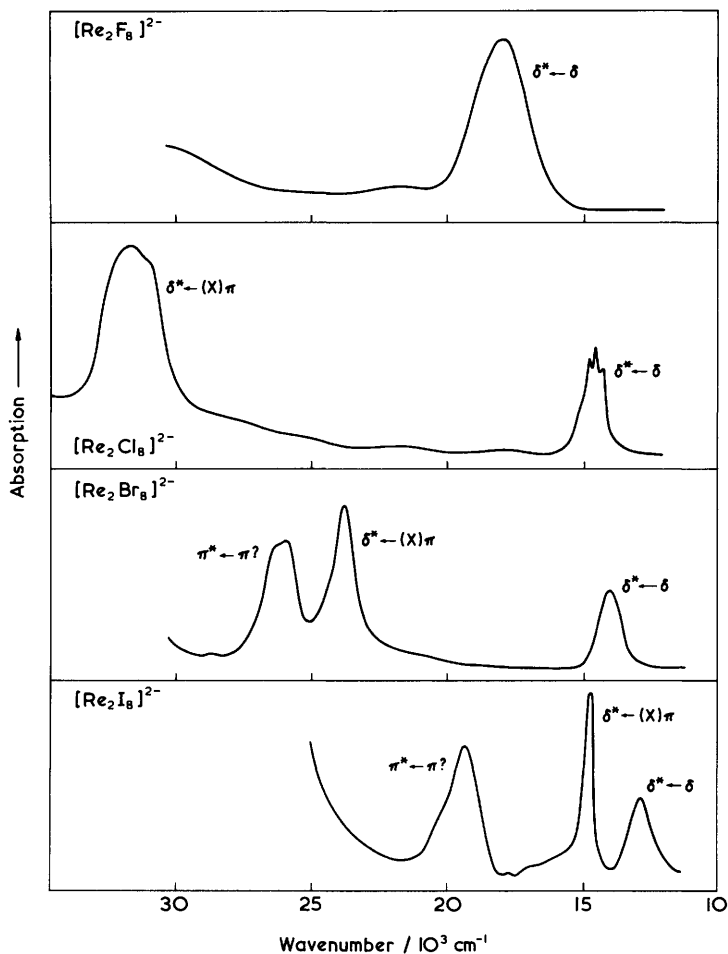


Figure 2. Electronic spectra of the complexes $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Re}_2\text{X}_8]$ at $\sim 14 \text{ K}$ in the region of their $\delta^* \leftarrow \delta$, $\delta^* \leftarrow \pi(X)$, and $\pi^* \leftarrow \pi(?)$ transitions (Cs[BF₄], KCl, KBr, and CsI discs for X = F, Cl, Br, or I, respectively)^{21,22}

of halogen character, and thus structural changes along both metal-metal and metal-halogen bond lengths would be expected, as implied by the RR results.

RR spectra of the sort described^{21,22} thus demonstrate that the nature of and assignments for electronic bands of structurally simple inorganic molecules can be made in a new and very convincing way. With some confidence, then, one could proceed to the study of larger, more structurally complex molecules.

²² R. J. H. Clark and M. J. Stead, *Inorg. Chem.*, 1983, **22**, 1214.

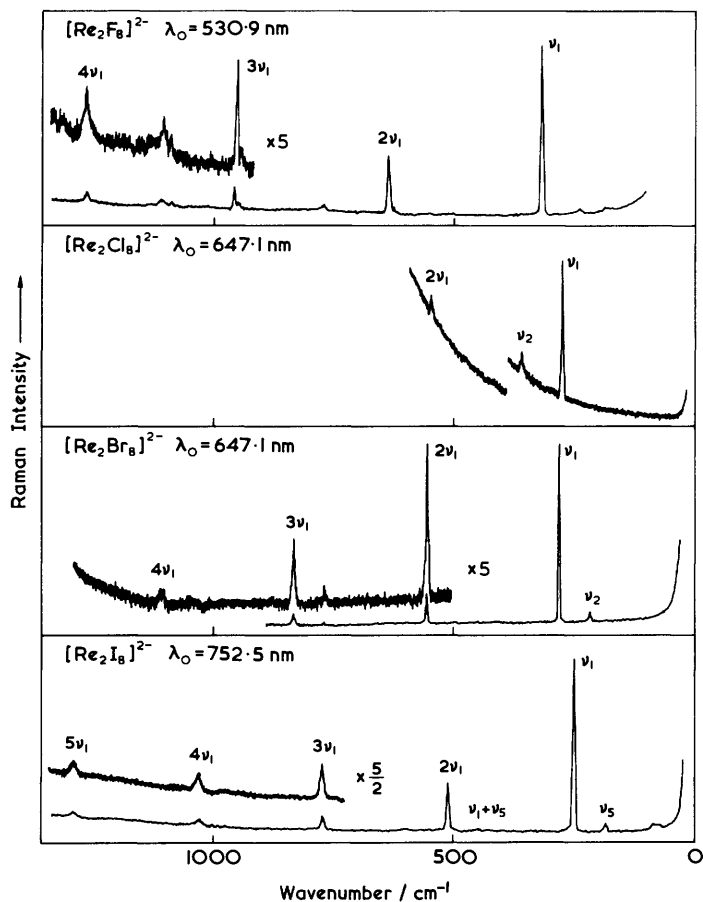


Figure 3 Resonance Raman spectra of the complexes $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Re}_2\text{X}_8]$ at ~ 80 K in the region of their $\delta^* \leftarrow \delta$ transitions^{21,22}

B. Rhodium–Rhodium Stretching Frequencies in Dirhodium Tetracarboxylates.—

The second problem in the area of metal–metal stretching frequencies to which attention will be drawn is the (until 1986) controversial one of the assignment of rhodium–rhodium stretching frequencies, $\nu(\text{RhRh})$, in dirhodium tetracarboxylate complexes. The initial indications of San Filippo and Sniadoch,²³ subsequently supported by Kharitonov *et al.*²⁴ and Kireeva *et al.*,²⁵ were in favour of the range $150\text{--}170\text{ cm}^{-1}$ for $\nu(\text{RhRh})$ in a variety of complexes of the type

²³ J. San Filippo and H. J. Sniadoch, *Inorg. Chem.*, 1973, **12**, 2326.

²⁴ Y. Y. Kharitonov, G. Ya. Mazo, and N. A. Knyazeva, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1970, **15**, 739.

²⁵ I. K. Kireeva, G. Ya. Mazo, and R. N. Shcheklov, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1979, **24**, 220.

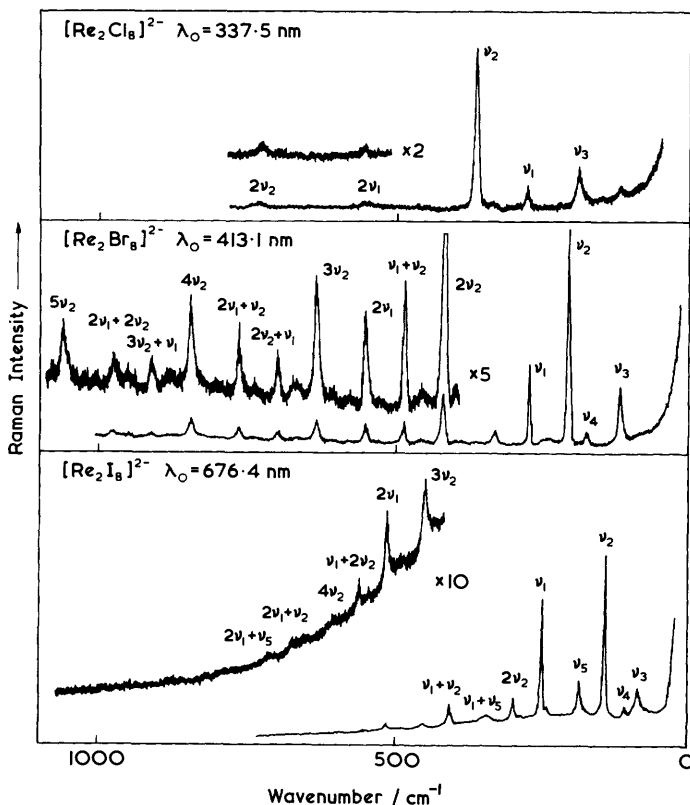


Figure 4 Resonance Raman spectra of the complexes $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Re}_2\text{X}_8]$ at ~ 80 K in the region of their $\delta^* \leftarrow \pi(\text{X})$ transitions^{21,22}

$\text{Rh}_2(\text{O}_2\text{CR})_4\text{L}_2$ (L = axial ligand). On the other hand Ketteringham and Oldham,²⁶ who also studied a range of complexes of this sort, favoured the range $288\text{--}351\text{ cm}^{-1}$ for $\nu(\text{RhRh})$. Raman and extensive electronic spectral analyses by Miskowski *et al.*²⁷ on $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$ and $\text{Li}_2\text{Rh}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ were based on the lower value for $\nu(\text{RhRh})$ and were given some theoretical basis as a result of molecular mechanics calculations.²⁸ Despite this wealth of research extending over 16 years there nevertheless appeared to be no firm evidence one way or the other regarding the correct wavenumber region of $\nu(\text{RhRh})$ in dirhodium tetracarboxylate complexes. It thus seemed highly desirable that detailed electronic, infrared, Raman, and resonance Raman studies of

²⁶ A. P. Ketteringham and C. J. Oldham, *J. Chem. Soc., Dalton Trans.*, 1973, 1067.

²⁷ V. M. Miskowski, W. P. Schaefer, B. Sadeghi, B. D. Santarsiero, and H. B. Gray, *Inorg. Chem.*, 1984, **23**, 1154.

²⁸ J. C. A. Boeyens, F. A. Cotton, and S. Han, *Inorg. Chem.*, 1985, **24**, 1750.

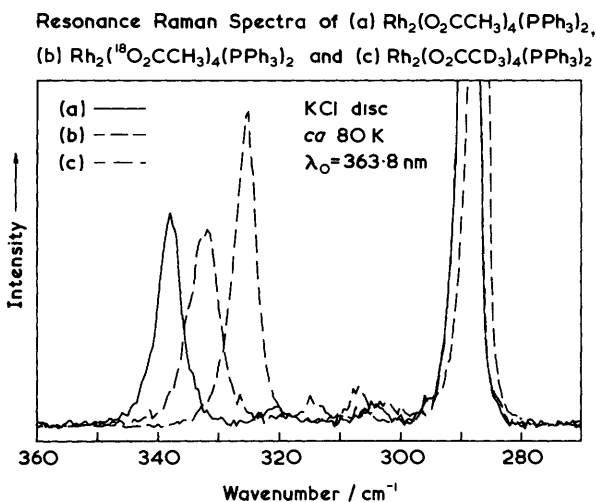


Figure 5 Resonance Raman spectrum of (a) $\text{Rh}_2(^{16}\text{O}_2\text{CCH}_3)_4(\text{PPh}_3)_2$, (b) $\text{Rh}_2(^{18}\text{O}_2\text{CCH}_3)_4(\text{PPh}_3)_2$, and (c) $\text{Rh}_2(^{16}\text{O}_2\text{CCD}_3)_4(\text{PPh}_3)_2$ as KCl discs at ca. 80 K ($\lambda_0 = 363.8 \text{ nm}$). The ν_1 bands are truncated in each case^{33,34}

$\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{PPh}_3)_2$ as its ^{16}O , ^{18}O , and CD_3 variants should be undertaken in order to resolve this problem definitively in one case at least. The choice of triphenylphosphine as axial ligand is advantageous for resonance Raman studies since the electric-dipole-allowed metal-based $\sigma \rightarrow \sigma^*$ transition of this complex (and of related ones) occurs in the near UV region and is accessible with Ar^{2+} 363.8 nm excitation. The HOMO is considered to be the a_{1g} (in D_{4h}) orbital with mainly Rh–Rh $d_\sigma - d_\sigma$ bonding but also some Rh–P $d_\sigma - n$ antibonding character. Raman spectra excited at resonance with electric dipole allowed transitions are usually much simpler than off-resonance spectra. Under these A -term conditions, it is only bands attributable to totally symmetric modes which are enhanced, together with bands attributable to overtones and combination tones involving the enhanced bands.^{11,12}

The resonance Raman spectra of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{PPh}_3)_2$ (Figure 5) convincingly demonstrate in the following way that $\nu(\text{RhRh})$ occurs at ca. 289 cm^{-1} . Any structural change attendant upon $\sigma \rightarrow \sigma^*$ excitation would be expected to occur primarily along the RhRh bond rather than along the virtually orthogonal RhO bonds. Hence it is $\nu(\text{RhRh})$ and its overtones which are expected to undergo the greatest intensification in a Raman spectrum taken at resonance with the $\sigma \rightarrow \sigma^*$ transition. The results indicate that it is the 289 cm^{-1} band which undergoes the resonance enhancement, and is thus to be assigned to ν_1 , $\nu(\text{RhRh})$. No band in the vicinity of 170 cm^{-1} appears in the spectra at all. Although $\nu(\text{RhP})$ might also be expected to be enhanced at resonance with the $\sigma \rightarrow \sigma^*$ transition it has not been positively identified. It could not be identified with ν_1 since this moves from 289.3 cm^{-1} to higher wavenumbers for

the analogous AsPh_3 and SbPh_3 derivatives (297 and 307 cm^{-1} , respectively), *i.e.* in the opposite direction to that expected on both mass and Rh–M bond-length grounds [for the complexes $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{MPh}_3)_2$, $r(\text{Rh}-\text{M})$ increases in the order RhP , 2.477 \AA , $< \text{RhAs}$, 2.576 \AA , $< \text{RhSb}$, 2.732 \AA].^{29,30} The axial nature of the resonant transition is confirmed by the fact that the depolarization ratio of the ν_1 band is $\frac{1}{3}$ at resonance.

The resonance Raman spectra of the ^{18}O and CD_3 analogues of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{PPh}_3)_2$ confirm this assignment convincingly. The most resonance-enhanced band, ν_1 , occurs at 289.3 , 289.1 , and 287.5 cm^{-1} for the ^{16}O , ^{18}O , and CD_3 derivatives, respectively, indicating the virtual independence of ν_1 of the equatorial modes, which is the situation to be expected for $\nu(\text{RhRh})$ since this coordinate is nearly orthogonal to $\nu(\text{RhO})$. On the other hand the two bands at 338.4 and 321 cm^{-1} in the resonance Raman spectrum of the ^{16}O complex are shifted by 6.4 and 7 cm^{-1} , respectively, to lower wavenumbers by ^{18}O substitution, consistent with the behaviour expected for modes in which the RhO stretching coordinate dominates (Figure 5). On deuteration, these modes move by rather more than this ($12\text{--}14\text{ cm}^{-1}$).

The combination of resonance Raman and isotopic work thus demonstrates conclusively that, for $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{PPh}_3)_2$, $\nu(\text{RhRh})$ is at 289.3 cm^{-1} . Since the RhRh bond length in this complex is $2.4505(2)\text{ \AA}$,²⁹ longer than in the analogous AsPh_3 [$2.427(1)\text{ \AA}$],³⁰ SbPh_3 [$2.421(4)\text{ \AA}$],³⁰ and H_2O [$2.3855(5)\text{ \AA}$]³¹ complexes, the implication is (in view of the expected reciprocal relationship between bond length and bond stretching frequency)³² that $\nu(\text{RhRh})$ in these complexes must all lie above 289.3 cm^{-1} , as indeed is found to be the case.^{33–35}

It is surprising at first sight that $\nu(\text{RhRh})$ has as high a value as it does in view of the fact that the $\text{Rh}-\text{Rh}$ bond (between the two d^7 ions) is only single. The high value is thought to arise from the significant contribution to the RhRh restoring force brought about by the four chelating acetate groups (primarily *via* the four OCO bending coordinates, which are coupled only in second order to the RhRh stretching coordinate). The results obtained provided a firm basis for making vibrational band assignments for other dirhodium tetracarboxylates, *viz.* $\text{Rh}_2(\text{O}_2\text{CR})_4(\text{PPh}_3)_2$, $\text{R} = \text{H}$, CH_3 , C_2H_5 , or C_3H_7 ,³⁶ and for $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4\text{L}_2$, $\text{L} = \text{H}_2\text{O}$ ³⁷ or $\text{S}(\text{CH}_2\text{Ph})_2$.³⁸

²⁹ G. G. Christoph, J. Halpern, G. P. Khare, Y. B. Koh, and C. Romanowski, *Inorg. Chem.*, 1981, **20**, 3029.

³⁰ R. J. H. Clark, A. J. Hempleman, H. M. Dawes, M. B. Hursthouse, and C. D. Flint, *J. Chem. Soc., Dalton Trans.*, 1985, 1775.

³¹ F. A. Cotton, B. G. DeBoer, M. D. LaPrade, J. R. Pival, and D. A. Ucko, *Acta Crystallogr., Sect. B*, 1971, **27**, 1664.

³² R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, 1965, **4**, 350.

³³ R. J. H. Clark, A. J. Hempleman, and C. D. Flint, *J. Am. Chem. Soc.*, 1986, **108**, 518.

³⁴ R. J. H. Clark and A. J. Hempleman, *Inorg. Chem.*, 1988, **27**, 2225.

³⁵ R. J. H. Clark and A. J. Hempleman, *Inorg. Chem.*, 1989, **28**, 746.

³⁶ R. J. H. Clark and A. J. Hempleman, *Inorg. Chem.*, 1989, **28**, 92.

³⁷ R. J. H. Clark and A. J. Hempleman, *Croat. Chem. Acta*, 1988, **61**, 313.

³⁸ R. J. H. Clark and A. J. Hempleman, *J. Mol. Struct.*, 1989, **197**, 105.

For certain of these complexes, e.g. $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{MPh}_3)_2$ $\text{M} = \text{P, As, or Sb}$, the geometric changes attendant upon excitation from the ground ($^1A_{1g}$) to the first excited ($^1A_{2u}$) state have been calculated³⁹ using the time-dependent theory of Tannor and Heller⁴⁰

Yet further resonance Raman studies of complexes of the same general structure have included those on tetracetamidates of the type $\text{Rh}_2(\text{CH}_3\text{-CONH})_4(\text{MPh}_3)_2$ and $\text{Rh}_2(\text{CF}_3\text{CONH})_4(\text{MPh}_3)_2$, $\text{M} = \text{P, As, or Sb}$, the tetraacetate to tetraacetamidate change for analogous complexes brings about an increase of ca 0.04 Å in the Rh–Rh bond length and a ca 15 cm^{-1} decrease in $\nu(\text{RhRh})$ ⁴¹

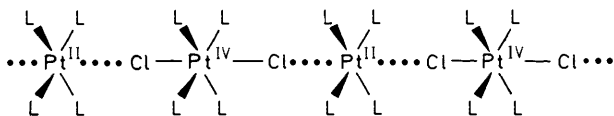
Similar studies of the diosmium(III) complexes $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$, $\text{Os}_2(\text{O}_2\text{-CCD}_3)_4\text{Cl}_2$, $\text{Os}_2(\text{O}_2\text{CCH}_2\text{Cl})_4\text{Cl}_2$, $\text{Os}_2(\text{O}_2\text{CC}_2\text{H}_5)_4\text{Cl}_2$, and $\text{Os}_2(\text{O}_2\text{CC}_3\text{H}_7)_4\text{Cl}_2$ have led to the identification of bands at 236–228, 393–256, and 311–292 cm^{-1} to $\nu(\text{OsOs})$, $\nu(\text{OsO})$, and $\nu(\text{OsCl})$, respectively^{42, 43}

These studies are illustrative of the ways in which $\nu(\text{MM})$ in metal–metal bonded dimers has been identified conclusively. Indeed, there is now a sufficiently firm basis for the assignments of $\nu(\text{MM})$ that corresponding assignments for bigger, especially linear-chain, complexes can now be made with some confidence

3 One-Dimensional Linear-Chain Complexes of Platinum, Palladium, and Nickel of the Wolfram's Red Type

A. Survey of the Structural Types, Physical Properties, and Spectroscopy.—Potassium tetracyanoplatinate, $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.30} \cdot 3\text{H}_2\text{O}$ (KCP) and its analogues are, on account of their being one-dimensional conductors, the best studied linear chain complexes of platinum⁴⁴. However, several other kinds of linear-chain complex have been the subject of much recent attention. In particular halogen-bridged linear-chain complexes of the platinum group, despite their having much lower conductivities than KCP, have proved to be of immense interest. Two types of such chain complex will be discussed, viz. the Wolfram's red (WR) type, where $\text{WR} = [\text{Pt}^{\text{II}}(\text{C}_2\text{H}_5\text{NH}_2)_4][\text{Pt}^{\text{IV}}(\text{C}_2\text{H}_5\text{NH}_2)_4\text{Cl}_2]\text{Cl}_4 \cdot 4\text{H}_2\text{O}$, and the type formed from the barrel-shaped complex ion $[\text{Pt}_2(\text{pop})_4]^{4-}$, where $\text{pop} = \text{diphosphite} = \text{H}_2\text{P}_2\text{O}_5^{2-}$

Complexes of the WR sort $[\text{PtL}_4][\text{PtL}_4\text{X}_2]\text{Y}_4$, have chain structures as indicated below



where L, a neutral equatorial ligand, may be an amine such as NH_3 , CH_3NH_2 ,

³⁹ K-S Shin, R J H Clark, and J I Zink *J Am Chem Soc* 1989, **111**, 4244

⁴⁰ D Tannor and E Heller, *J Phys Chem*, 1982, **77**, 202

⁴¹ S P Best, P Chandley, R J H Clark, S McCarthy, M B Hursthouse, and P A Bates *J Chem Soc, Dalton Trans*, 1989, 581

⁴² R J H Clark, A J Hempleman and D A Tocher, *J Am Chem Soc* 1988 **110** 5968

⁴³ R J H Clark and A J Hempleman, *J Chem Soc, Dalton Trans* 1988 2601

or $C_2H_5NH_2$ and $X = Cl, Br, \text{ or } I$. Bidentate ligands LL can also form complexes of this general structural type, where LL may be 1,2-diaminoethane (en), 1,2-diaminopropane (pn), 1,3-diaminopropane (tn), *etc.* Moreover, both terdentate ligands, LLL, such as diethylenetriamine (dien) and *N*-methyl-diethylenetriamine (Medien), and quadridentate ligands, LLLL, such as 1,4,8,11-tetraazacyclotetradecane (cyclam) will also form complexes of this general type.⁴⁵ WR consists of Pt^{II} and Pt^{IV} units, each of which bears a +2 charge, and hence four anions are required for electroneutrality. In addition to this type of complex, however, chain complexes of the same basic structure can also be formed in which the equatorial amine ligands are replaced by one, two, three, or four halide ions, with the result that the overall charge must be balanced by two, zero, two, or four counter ions, respectively, *e.g.* as in $[Pt^{II}(\text{Medien})I][Pt^{IV}(\text{Medien})I_3]I_2$, $[Pt^{II}(\text{en})Cl_2][Pt^{IV}(\text{en})Cl_4]$, $K_2[Pt^{II}(\text{NH}_3)Cl_3][Pt^{IV}(\text{NH}_3)Cl_5] \cdot 2H_2O$, and $K_4[Pt^{II}I_4][Pt^{IV}I_6]$, respectively. The counter ions may be Cl^- , Br^- , I^- , ClO_4^- , BF_4^- , NO_3^- , K^+ , or Cs^+ *etc.*; they play an important role, often along with water of crystallization, in helping to hold the chains together by hydrogen bonding. A summary of the different types of M^{II}/M^{IV} linear-chain-complexes of the +2, +2 type now known is given in Figure 6.

The intense colours of linear-chain complexes, which differ markedly from those of their constituent platinum(II) and (IV) entities, are caused by intervalence (IVCT) transitions $Pt^{II} \longrightarrow Pt^{IV}$, which are polarized in the chain direction; they occur in the regions 25 000—18 200 cm^{-1} ($X = Cl$), 23 600—14 300 cm^{-1} ($X = Br$), and 20 600—7 500 cm^{-1} ($X = I$). Extensive research has established that the shorter the $Pt^{II} \cdots Pt^{IV}$ chain distance, the lower in wavenumber is the intervalence transition. This is consistent with the idea that shortening of the chain repeat unit is primarily brought about by a shortening of the $Pt^{II} \cdots X$ rather than the $Pt^{IV}-X$ distance, resulting in more nearly central bridging by the chain halide. Central halide bridging is known also to be critical in bringing about increased chain conductivity. In addition to IVCT transitions, the complexes display luminescence with a large Stokes shift.⁴⁶

The Raman spectra of halogen-bridged mixed-valence complexes of platinum at resonance with the $Pt^{II} \longrightarrow Pt^{IV}$ intervalence band are very intense. In particular, the band attributed to the symmetric $X-Pt^{IV}-X$ chain stretching mode (ν_1), together with those attributed to long overtone progressions $\nu_1\nu_1$, are tremendously enhanced at resonance. The overtone progressions reach as far as $17\nu_1$ in some cases (Figure 7), implying a very substantial (0.05—0.10 Å) change in $Pt^{IV}-Cl$ bond length on changing from the ground to the intervalence state;^{11,12,47} this structural change constitutes, in effect, a reverse Peierls

⁴⁴ M. B. Robin and P. Day, in 'Advances in Inorganic and Radiochemistry', ed. H. J. Emeléus and A. G. Sharpe, Academic Press, New York, Vol. 10, 1967, p. 247.

⁴⁵ R. J. H. Clark, *Chem. Soc. Rev.*, 1984, 13, 219. R. J. H. Clark, in 'Advances in Infrared and Raman Spectroscopy', ed. R. J. H. Clark and R. E. Hester, Wiley/Heyden, Chichester, Vol. 11, 1984, p. 95; R. I. Buckley and R. J. H. Clark, *Coord. Chem. Rev.*, 1985, 65, 167.

⁴⁶ H. Tanino and K. Kobayashi, *J. Phys. Soc. Japan*, 1983, 52, 1446.

⁴⁷ R. J. H. Clark, M. Kurmoo, H. J. Keller, B. Kepler, and U. Traeger, *J. Chem. Soc., Dalton Trans.*, 1980, 2498.

Synthesis, Structure, and Spectroscopy of Metal–Metal Dimers, Linear Chains, etc.

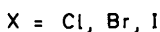
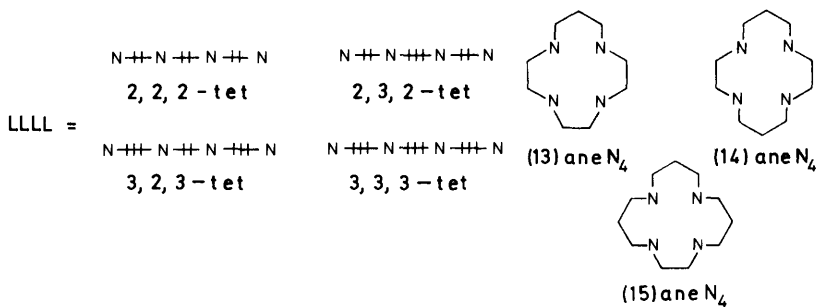
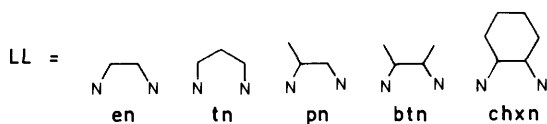
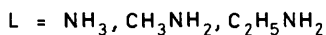
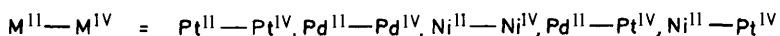


Figure 6 Summary of the known M^{II}/M^{IV} linear-chain complexes of the types $[ML_4][ML_4X_2]Y_4$, $[M(LL)_2][M(LL)_2X_2]Y_4$, and $[M(LLLL)][M(LLLL)X_2]Y_4$

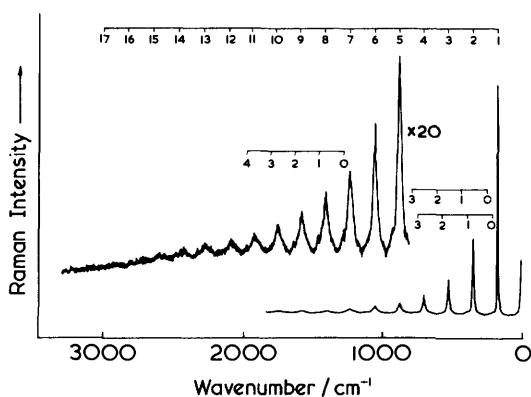


Figure 7 Resonance Raman spectrum of $[Pt(pn)_2][Pt(pn)_2Br_2][Cu_3Br_5]_2$, pn = 1,2-propanediamine, in a KBr disc at ca. 80 K with 568.2 nm excitation⁴⁷

transition. The relationship between Peierls energy gaps and lattice distortions has been discussed by Whangbo and Foshee.⁴⁸

The ν_1 values (for ν_0 at resonance with the intervalence transition) range from 309.1—297.8 cm^{-1} ($X = \text{Cl}$), 175.7—172.0 cm^{-1} ($X = \text{Br}$), and 122.3—114.2 cm^{-1} ($X = \text{I}$). Recent synthetic, spectroscopic, and structural work has led to the characterization of structurally analogous palladium complexes as well as mixed-metal derivatives of the sort $[\text{Ni}^{\text{II}}(\text{en})_2][\text{Pt}^{\text{IV}}(\text{en})_2\text{Cl}_2][\text{ClO}_4]_4$, $[\text{Pd}^{\text{II}}(\text{en})_2][\text{Pt}^{\text{IV}}(\text{en})_2\text{Cl}_2][\text{ClO}_4]_4$, and analogous 1,2-diaminopropane complexes.^{49–51}

Doubt existed for some years as to whether mixed-valence nickel(II,IV) complexes of the same structural type existed.^{52–54} Characterization of such complexes had been complicated by difficulties experienced in growing single crystals and also by crystallographic disorder. However, their characterization is now certain on the basis of careful synthetic, conductivity, electronic, and photoelectron spectroscopy, EXAFS, X -ray structural, magnetic, and other work, in particular that of Toriumi, Yamashita *et al.*^{55–60} Such complexes are black, the deep colour being attributed to the $\text{Ni}^{\text{II}} \rightarrow \text{Ni}^{\text{IV}}$ intervalence transition centred on *ca.* 15 000 cm^{-1} for a chloride-bridged species. The wavenumbers of the intervalence band maxima of given equatorial ligands vary in the order $\text{Cl} > \text{Br} > \text{I}$, and $\text{Pd}^{\text{II}}/\text{Pt}^{\text{IV}} > \text{Ni}^{\text{II}}/\text{Pt}^{\text{IV}} > \text{Pt}^{\text{II}}/\text{Pt}^{\text{IV}} > \text{Pd}^{\text{II}}/\text{Pd}^{\text{IV}} > \text{Ni}^{\text{II}}/\text{Ni}^{\text{IV}}$.^{45,57,60} The result implies that the valence electrons of linear-chain $\text{M}^{\text{II,IV}}$ complexes are most delocalized for those of $\text{Ni}^{\text{II}}/\text{Ni}^{\text{IV}}$, an implication in agreement with the fact that the (pellet) electrical conductivity of linear-chain $\text{Ni}^{\text{II}}/\text{Ni}^{\text{IV}}$ complexes ($\sigma(300 \text{ K}) \sim 10^{-7} \Omega^{-1} \text{ cm}^{-1}$) is much greater than those of analogous linear-chain complexes of platinum or palladium with the same bridging halogen atoms. Nevertheless, the chain conductivity even of $\text{Ni}^{\text{II}}/\text{Ni}^{\text{IV}}$ complexes is low, a matter which is clearly linked to the fact that the bridging atom is not centrally placed. The conductivity of such complexes is well represented by the expression $\sigma(T) = \sigma_0 \exp(-\Delta E/kT)$; thus for $[\text{Ni}(\text{en})_2][\text{Ni}(\text{en})_2\text{Cl}_2]\text{Cl}_4$, the $\sigma(300 \text{ K}) \sim 6 \times 10^{-8} \Omega^{-1} \text{ cm}^{-1}$ and ΔE (the thermal activation energy) $\sim 0.5 \text{ eV}$.⁵⁶ Speculation as to whether or not a symmetrically bridged chain complex might be stable was recently resolved in the affirmative.

⁴⁸ M.-H. Whangbo and M. J. Foshee, *Inorg. Chem.*, 1981, **20**, 113.

⁴⁹ R. J. H. Clark and V. B. Croud, *Inorg. Chem.*, 1984, **24**, 588; 1986, **25**, 1751.

⁵⁰ R. J. H. Clark, V. B. Croud, and R. J. Wills, *Inorg. Chem.*, 1988, **27**, 2096.

⁵¹ R. J. H. Clark, V. B. Croud, R. J. Wills, P. A. Bates, H. M. Dawes, and M. B. Hursthouse, *Acta Cryst., Sect. B*, 1989, **45**, 147.

⁵² M. Yamashita, Y. Nonaka, S. Kida, Y. Hamaue, and R. Aoki, *Inorg. Chim. Acta*, 1981, **52**, 43.

⁵³ G. C. Papavassiliou and D. Layek, *Z. Naturforsch., Teil B*, 1982, **37**, 1406.

⁵⁴ D. A. Cooper, S. J. Higgins, and W. Levason, *J. Chem. Soc., Dalton Trans.*, 1983, 2131.

⁵⁵ M. Yamashita and T. Ito, *Inorg. Chim. Acta*, 1984, **87**, L5; M. Yamashita and I. Murase, *Inorg. Chim. Acta*, 1985, **97**, L43.

⁵⁶ M. Yamashita, I. Murase, I. Ikemoto, and T. Ito, *Chem. Lett.*, 1985, 1133.

⁵⁷ Y. Wada, T. Mitani, M. Yamashita, and T. Koda, *J. Phys. Soc. Japan*, 1985, **54**, 3143; M. Yamashita, I. Murase, T. Ito, Y. Wada, T. Mitani, and I. Ikemoto, *Bull. Chem. Soc. Japan*, 1985, **58**, 2336.

⁵⁸ K. Toriumi, T. Kanao, Y. Umetsu, A. Ohyoshi, M. Yamashita, and T. Ito, *J. Coord. Chem.*, 1988, **19**, 209.

⁵⁹ J. Evans, J. T. Gauntlett, and W. Levason, *Inorg. Chem.*, 1988, **27**, 4523 and references therein.

⁶⁰ K. Toriumi, Y. Wada, T. Mitani, S. Bandow, M. Yamashita, and Y. Fujii, *J. Am. Chem. Soc.*, 1989, **111**, 2341; Y. Wada, T. Mitani, K. Toriumi, and M. Yamashita, *J. Phys. Soc. Japan*, 1989, **58**, 3013.

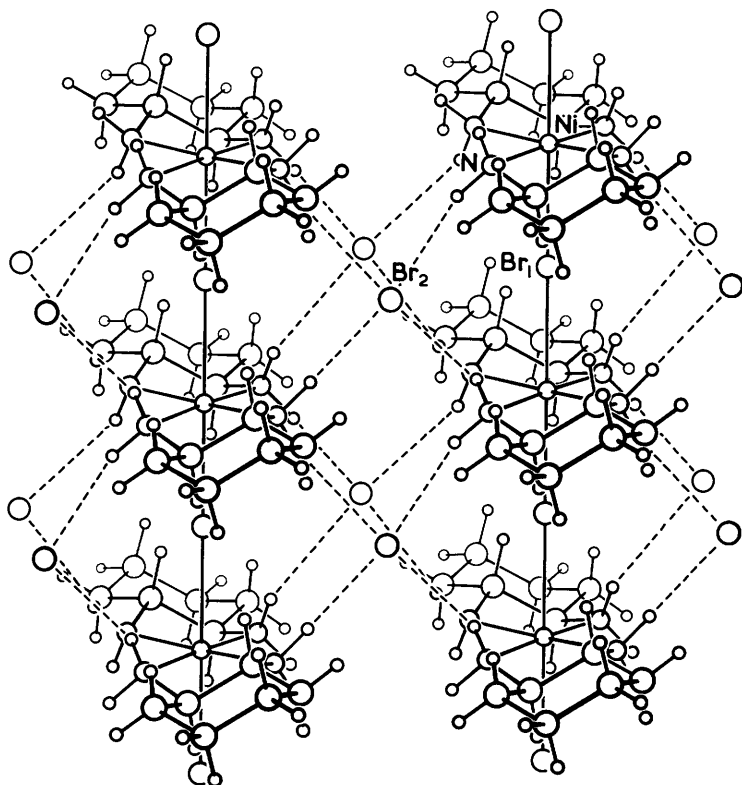


Figure 8 X-ray crystal structure of $[\text{Ni}(\text{R,R-chxn})_2\text{Br}]\text{Br}_2$ showing the environment of the bromide ions. The dashed lines indicate the orientation of the hydrogen bonds⁶⁰

This matter and two others of great contemporary interest are now discussed in more detail

B. Symmetrically Bridged Chain Complexes of Nickel.—Nickel complexes of the sort $[\text{Ni}(\text{R,R-chxn})_2\text{Cl}]\text{Cl}_2$ (red) and $[\text{Ni}(\text{R,R-chxn})_2\text{Br}]\text{Br}_2$ (black) can be formed by oxidation of $\text{Ni}(\text{R,R-chxn})_2\text{X}_2$ with Cl_2/N_2 or Br_2/N_2 , respectively, in 2-methoxyethanol to form semi-conducting complexes in which the bridging group is centrally positioned⁶⁰ The low temperature (-151°C) structure, with very small thermal ellipsoids, thus provides no evidence for the expected Peierls distortion of the linear chain. Presumably, exceptionally effective hydrogen bonding prevents this distortion from taking place. Indeed the complexes have in effect two- rather than one-dimensional character on account of strong hydrogen bonding not only in the chain direction but also in one of the two directions perpendicular to the chains (Figure 8). Central bridging has the effect of increasing the chain conductivity by $ca\ 10^3$

Conductivity and other properties of these cyclohexanediamine complexes are

Table 1 Properties of symmetric chain nickel complexes

Complex	$\sigma/\Omega^{-1} \text{ cm}^{-1}$	Activation energy/eV	Energy gap/eV
$[\text{Ni}(\text{R,R-chxn})_2\text{Cl}]\text{Cl}_2$	10^{-3}	0.19	1.9
$[\text{Ni}(\text{R,R-chxn})_2\text{Br}]\text{Br}_2$	2×10^{-2}	0.11	1.28

Table 2 Variants of Nickel(III) Complexes

Discrete Ni^{III} complex: $[\text{Ni}([\text{14-aneN}_4)\text{Cl}_2][\text{ClO}_4]$, $[\text{14-aneN}_4 = \text{cyclam (or } 2 \times \text{en})$
 Ni^{II} complex coordinated to cation radicals: $[\text{NiCl}_2(\text{diars})_2]\text{Cl}$, diars = *o*-phenylene bis-dimethylarsine
 $\text{Ni}^{\text{II}}/\text{Ni}^{\text{IV}}$ 1D-chain complex: $[\text{Ni}(\text{en})_2][\text{Ni}(\text{en})_2\text{Cl}_2][\text{ClO}_4]$, en = 1,2-diaminoethane
 Symmetrical 1D-chain Ni^{III} complex: $[\text{Ni}(\text{R,R-chxn})_2\text{Br}]\text{Br}_2$, chxn = cyclohexanediamine
 Partially oxidized Ni^{II} 1D-complex: $\text{Ni}(\text{Hdpg})_2\text{I} \equiv [\text{Ni}(\text{Hdpg})_2]_5\text{I}_5$, a $\text{Ni}^{2.2}$ complex involving I_5^-

given in Table 1. Despite the fact that much consideration has been given to the matter, the mechanism for the conductivity of all such chain complexes is not yet clear. Raman spectroscopy of the bromo complex shows no clear evidence of a ν_1 band (or of its overtone bands), consistent with the behaviour expected for a centrally bridged halide.⁶¹ The bromo complex is nearly diamagnetic, which implies that there is a strong antiferromagnetic coupling of the unpaired electrons ($s = \frac{1}{2}$) in the d_{z^2} orbitals located on each nickel atom.

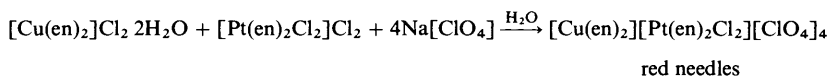
It is worth noting that there are many different sorts of apparent nickel(III) complexes, in only some of which the metal is genuinely in this oxidation state (Table 2). The most obvious are the *trans*-octahedral discrete species $[\text{Ni}([\text{14-aneN}_4)\text{Cl}_2][\text{ClO}_4]$ and $[\text{Ni}(\text{en})_2\text{Cl}_2][\text{ClO}_4]$. Others apparently of this sort, e.g. $[\text{Ni}(\text{diars})_2\text{Cl}_2]\text{Cl}$, are thought likely to contain nickel(II) coordinated to a cation radical derived from *o*-phenylenebisdimethylarsine; however, this conclusion seems uncertain in the case of the analogous diamine.^{52,59} The nickel(II,IV) complexes are, of course, variants on the nickel(III) formulation, which is only strictly realized for the two complexes for which it is established that the bridging atom is centrally positioned. The final variant, $\text{Ni}(\text{Hdpg})_2\text{I}$, where H_2dpg = diphenylglyoxime, is not a complex of nickel(III) but one of $\text{Ni}^{2.2}$ since the counterion is not I^- but I_5^- .⁶²

C. Copper(II)/Platinum(IV) Linear-Chain Complexes.—It is interesting to investigate the possibility of inserting other metals of the first transition series into the site of the bivalent metal in linear-chain complexes. In this context the

⁶¹ K. Toriumi, H. Okamoto, T. Mitani, S. Bandow, M. Yamashita, Y. Fujii, R. J. H. Clark, D. J. Michael, A. J. Edward, D. Watkin, M. Kurmoo, and P. Day, *Mol. Cryst. Liq. Cryst.*, 1990, in press.

⁶² M. Cowie, A. Gleizes, G. W. Grynkewich, D. W. Kalina, M. S. McClure, R. P. Scaringe, R. C. Teitelbaum, S. L. Ruby, J. A. Ibers, C. R. Kannewurf, and T. J. Marks, *J. Am. Chem. Soc.*, 1979, **101**, 2921.

following reaction between copper(II) and platinum(IV) complexes has been reported⁶³



The complex is isomorphous with $[\text{M}(\text{en})_2][\text{M}(\text{en})_2\text{Cl}_2][\text{ClO}_4]_4$ $\text{M} = \text{Pd}$ or Pt , $\text{X} = \text{Cl}$ or Br , and thus the bridging chlorine atom (as is usually the case for such complexes) is positionally disordered at two sites equidistant from the midpoint between the two metal atom sites and with an occupancy of 0.5. The Cu^{II} and Pt^{IV} ions are also disordered at the metal ion sites and thus cannot be distinguished from one another. Nevertheless, the structure has been established and found to have $r(\text{Cu}^{\text{II}}-\text{Cl}) = 3.081 \text{ \AA}$ and $r(\text{Pt}^{\text{IV}}-\text{Cl}) = 2.313 \text{ \AA}$. Difficulties arising from partial substitution of Cu^{II} by Pt^{IV} during preparation⁶³—leading to a reported Pt/Cu ratio of 1.11089—can be overcome by rapid rather than slow growth of crystals⁶⁴.

The magnetic susceptibility ($C = 0.415 \text{ emu mol}^{-1} \text{ K}$) of the complex obeys the Curie–Weiss law ($\theta = -1.2 \text{ K}$) and the ESR spectrum ($g_{\perp} = 2.048$, $g_{\parallel} = 2.167$, \parallel relating to the chain direction) implies that there is no significant magnetic interaction between the unpaired electrons occupying the $d_{x^2-y^2}$ orbitals on the copper (d^9) ions which are $\sim 10.8 \text{ \AA}$ apart along the chains⁶³. This situation is thus in contrast with that for Ni^{III} chain complex (*vide supra*) in which the unpaired electrons occupy d_{z^2} orbitals and interact so strongly as to render the complex antiferromagnetic, almost diamagnetic.

Contrary to the earlier report,⁶³ the lack of dichroism and resonance Raman progressions involving the $\nu(\text{Cl}-\text{Pt}^{\text{IV}}-\text{Cl})$ mode using visible excitation suggests that the intervalence transition in this complex is in the ultra-violet, the red colour being caused by local transitions on the copper(II) moieties⁶⁴.

Several attempts have been made to introduce other heavy metals into the chains but to date the only success in this respect is with gold, the complex $[\text{Au}_x\text{Pt}_{1-x}(\text{en})_2]\text{SO}_4 \cdot 3\text{H}_2\text{O}$, $x = 0.03$, having been prepared⁶⁵.

D. Structure to the ν_1 Band of Linear-Chain Complexes.—One of the more surprising discoveries made in 1983 was that the wavenumber of ν_1 , $\nu_{\text{sym}}(\text{XPtX})$, in linear-chain complexes appears, under conditions of only moderate resolution, to increase as that of the exciting line (ν_0) increases⁶⁶. This apparent dispersion in ν_1 is very evident when seen against the backdrop of bands attributed to amine modes, which show virtually no dispersion. For any particular set of complexes, the apparent shift in ν_1 increases in the order $\text{Cl} < \text{Br} < \text{I}$, and is largest for those in which the bond length ratio $r(\text{Pt}^{\text{IV}}-\text{X})/r(\text{Pt}^{\text{II}}-\text{X})$ is nearest to

⁶³ H. Oshio, K. Torumi, S. Bandow, K. Miyagawa and S. Kurita, *J. Chem. Soc. Dalton Trans.* 1990, 1013.

⁶⁴ R. J. H. Clark, D. J. Michael and M. Yamashita, to be published.

⁶⁵ N. Matsushita, N. Kojima, T. Ban and I. Tsujikawa, *J. Phys. Soc. Japan* 1987, **56**, 3808.

⁶⁶ R. J. H. Clark and M. Kurmoo, *J. Chem. Soc. Faraday Trans. 2* 1983, **79**, 519.

unity (usually iodine-chain complexes) and in which the $\text{Pt}^{\text{II}} \cdots \text{Pt}^{\text{IV}}$ distance is least (brought about by strong hydrogen-bonding between the amines of different chains and the counter ion). The magnitude of the apparent dispersion to ν_1 can be as much as 20 cm^{-1} .

Careful, high resolution studies of these complexes as single crystals at low temperatures and by use of low laser powers have now shown that the dispersion in ν_1 is only apparent; it is caused by the fact that the ν_1 band consists of many, closely spaced, components, those of higher wavenumber being resonance enhanced with excitation lines of higher wavenumber. If wider slits or more power is used, only the overall contour of the ν_1 band is detected, which accordingly disperses as the relative intensities of its components change.⁶⁷⁻⁷⁰

The origin of the components to ν_1 is still a matter for debate. At the moment, the most likely explanation is that each component arises from a chain segment of different correlation length (defined as the length over which the oxidation states alternate II and IV regularly and without defects of any sort). Each segment has slightly different wavenumbers for ν_1 , its IVCT band maximum, and its excitation profile maximum, from the corresponding values for other segments. Since shorter segments in conjugated polyenes are known to give rise to higher ν_1 values and to higher values for the absorption band maxima, it is presumed that these same features will hold true for linear-chain metal complexes. This explanation of the apparent dispersion in ν_1 thus requires postulation of the existence of a certain small distribution of discrete but relatively short correlation lengths within each chain; each segment (or small group of segments) can thus be made, in turn, to come into resonance as ν_0 is changed, leading (where the resolution is moderate) to the apparent dispersion of the overall ν_1 band contour with change of ν_0 .

Somewhat analogous behaviour has also been observed for certain bands (e.g. $\nu(\text{C}=\text{C})$ and $\nu(\text{C}-\text{C})$ at ~ 1450 and 1060 cm^{-1} , respectively) of *trans*-polyacetylene, $(\text{CH})_x$ and $(\text{CD})_x$.⁷¹⁻⁷⁵ These bands likewise exhibit an apparent dependence of their wavenumber on ν_0 , an observation which has been attributed in this case also to the existence of segments within each chain of different correlation lengths. Such segments are likewise expected to possess different wavenumbers for ν_1 , the absorption band maxima, and excitation profile maxima. Change of ν_0 will selectively enhance different components to ν_1 leading, if the components are not resolved, to dispersion in the overall ν_1 band contour with change of ν_0 . Why segments of only certain lengths should be

⁶⁷ R. J. H. Clark and V. B. Croud, *J. Phys. C: Solid State Phys.*, 1986, **19**, 3467.

⁶⁸ M. Tanaka and S. Kurita, *J. Phys. C: Solid State Phys.*, 1986, **19**, 3019.

⁶⁹ S. D. Conradson, R. F. Dallinger, B. I. Swanson, R. J. H. Clark, and V. B. Croud, *Chem. Phys. Lett.*, 1987, **135**, 463.

⁷⁰ R. J. H. Clark and D. J. Michael, *J. Mol. Struct.*, 1988, **189**, 173.

⁷¹ H. Kuzmany and P. Kröll, *J. Raman Spectrosc.*, 1986, **17**, 89.

⁷² Z. Vardeny, J. Ornstein, and G. L. Baker, *Phys. Rev. Lett.*, 1983, **50**, 2032.

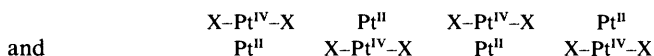
⁷³ Z. Vardeny, E. Ehrenfreund, O. Brafman, and B. Horovitz, *Phys. Rev. Lett.*, 1983, **51**, 2326.

⁷⁴ R. Tiziani, G. P. Brivio, and E. Mulazzi, *Phys. Rev. B*, 1985, **31**, 3019.

⁷⁵ A. W. Tarr and W. Siebrand, *J. Raman Spectrosc.*, 1989, **20**, 209.

formed, however, is far from clear, a consideration which undermines confidence in the proposed explanation for the dispersion (both for $(\text{CH})_x$ as well as for Wolfram's red salts)

The better understanding of the nature and properties of the segments giving rise to the discrete components to ν_1 —thought to be linked closely to the properties of solitons and polarons^{76–79}—is important to the understanding of the structures, spectral properties, and conductivity mechanisms displayed by both Wolfram's red type complexes as well as *trans*-polyacetylene. Indeed, there are many similarities between these two, otherwise disparate, systems, hinging around the fact that the former has a centre of inversion at each metal atom while the latter has one at the middle of each double and single bond⁸⁰. Since in each case there is two-fold degeneracy the possibility that each might support the existence of solitons (domain walls) seems likely. Thus, the valence bond structures



are equivalent in an infinite chain, translating from one to the other by a concerted movement of the X-atoms away from Pt^{IV} towards Pt^{II} with an interchange of oxidation states. Likewise



are equivalent and may be interconverted by a concerted lengthening and shortening of the C–C bonds accompanied by a transfer of electron density between the bonds. The soliton and polaron analogies between *trans*-polyacetylene and Wolfram's red salts are illustrated in Figure 9.

Apart from defects occurring as intrinsic features in crystals of Wolfram's red salts, as grown, defects may also be generated *via* impurity doping, high pressures,^{81, 82} or photoexcitation. Increased concentrations of defects lead to much enhanced chain conductivities. Thus, iodine doping of $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{I}_2][\text{ClO}_4]_4$ leads to an increase in the chain conductivity of this complex of over 10^7 . The absorbance of two mid-gap bands (at *ca* 1.65 and 1.98 eV)⁸³ and the ESR intensity in dilute doped crystals increase with dopant concentration. Thus low levels of halogen doping have the same effects on optical absorption.

⁷⁶ N Kuroda, M Sakai, and Y Nishina, *Phys Rev Lett*, 1987, **58**, 2122

⁷⁷ S Kurita, M Haruki, and K Miyagawa, *J Phys Soc Japan*, 1988, **57**, 1789

⁷⁸ Y Onadera, *J Phys Soc Japan*, 1987, **56**, 250

⁷⁹ J T Gammel, R J Donohue, A R Bishop, and B I Swanson, to be published

⁸⁰ P Day, Discussion comment, *Phil Trans Roy Soc Lond*, 1985, **A314**, 144. P Day, in 'Organic and Inorganic Low-Dimensional Crystalline Materials', ed P Delhaes and M Drillon, NATO ASI Series B Physics, 1987, vol 168, p 33. See also R J H Clark and V B Croud, *idem*, p 341

⁸¹ B I Swanson, M A Stroud, S D Conradson, and M H Zietlow, *Solid State Comm*, 1988, **65**, 1405

⁸² M A Stroud, H G Drickamer, M H Zietlow, H B Gray, and B I Swanson, *J Am Chem Soc*, 1989, **111**, 66

⁸³ S Kurita, M Haruki, and K Miyagawa, *J Phys Soc Japan*, 1988, **57**, 1789

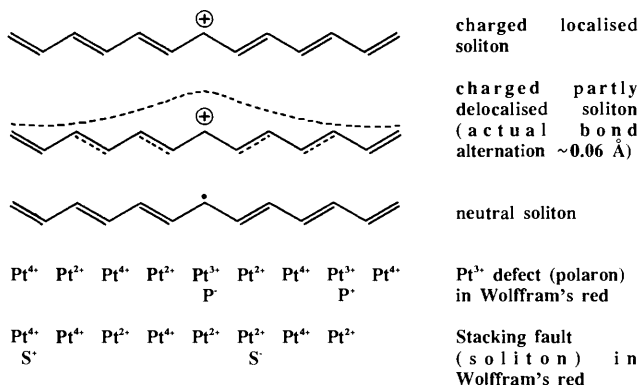


Figure 9 Soliton and polaron analogies between trans-(CH)_x and Wolfram's red

spectra and ESR spectra as does photoexcitation using radiation with its electric vector parallel to the chain axis at a wavenumber greater than or equal to that of the IVCT transition. The origin of the defects is thought to be the same in each case. Doping-induced states are located on single chains and have both charge and spin, suggesting that they are polarons.⁸⁴ Photoinduced defects occur as a result of separation of the electron-hole pairs created by the IVCT transition.

Extensive theoretical discussions of the potential energy surfaces of Wolfram's red type complexes have been given by Nasu and Toyazawa^{85,86} and more recently, by Prassides, Day *et al.*⁸⁷ Both the resonance Raman band profiles as well as those of the intense emission at about half the bandgap have been successfully modelled. The reader is referred elsewhere for a discussion of this treatment.⁸¹ Many other studies of these intriguing complexes are currently under study, particularly related to the full understanding of their luminescence and its dependence on pressure.⁸⁸

4 Diphosphite Complexes

The synthesis of two barrel-shaped ions [Pt₂(H₂P₂O₅)₄]⁴⁻ and [Pt₂(H₂P₂O₅)₄Cl₂]⁴⁻,^{89,90} the properties of which (for X = Cl) are given in Figure 10, posed the intriguing question as to whether or not the ions could be induced to co-crystallize to form a stacked chain complex directly analogous to Wolfram's red. Here the ligand bridging the platinum atoms is the diphosphite

⁸⁴ M. Haruki and S. Kurita, *J. Phys. Rev. B.*, 1989, **39**, 5706.

⁸⁵ K. Nasu, and Y. Toyazawa, *J. Phys. Soc. Japan*, 1982, **51**, 2098.

⁸⁶ K. Nasu, *J. Phys. Soc. Japan*, 1983, **52**, 3865; *ibid.*, 1984, **53**, 427; *ibid.*, 1985, **54**, 1933.

⁸⁷ K. Prassides, P. N. Schatz, K. Y. Wong, and P. Day, *J. Phys. Chem.*, 1986, **90**, 5588.

⁸⁸ H. Tanino, N. Koshizuka, K. Kobayashi, M. Yamashita, and K. Hoh, *J. Phys. Soc. Japan*, 1985, **54**, 483.

⁸⁹ R. P. Sperline, M. K. Dickson, and D. M. Roundhill, *J. Chem. Soc., Chem. Commun.*, 1977, 62.

⁹⁰ M. A. Filomena Das Remedios Pinto, P. J. Sadler, S. Neidle, M. R. Sanderson, and A. Subbiah, *J. Chem. Soc., Chem. Commun.*, 1980, 13.

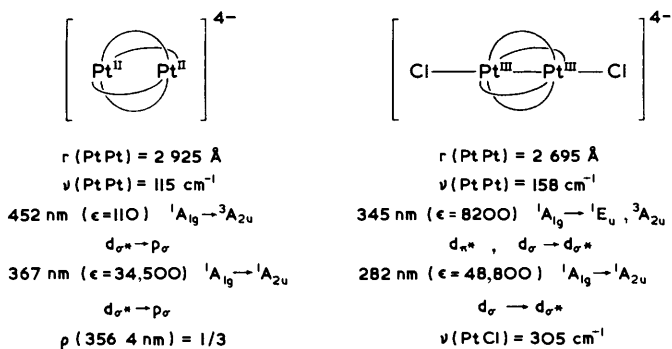


Figure 10 Spectroscopic and structural properties of the complex ions $[\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4]^{4-}$ and $[\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4\text{Cl}_2]^{4-}$

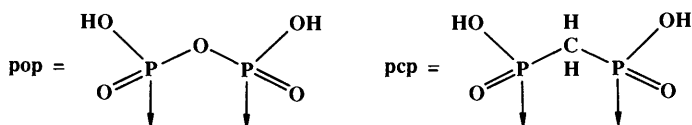


Figure 11 Diphosphate ligands

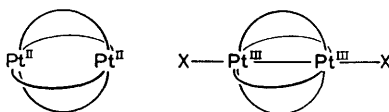


Figure 12 Schematic representation of the chain structure of $\text{K}_4[\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4\text{Cl}]\cdot 3\text{H}_2\text{O}^{95}$

$\text{H}_2\text{P}_2\text{O}_5^{2-}$ (pop, Figure 11). This synthesis has, indeed, proved to be possible,^{91–94} as indicated schematically in Figure 12 (with pop as the ligand). A more detailed view of one repeat unit along the chain is given in Figure 13, which also shows the two equivalent positions for the bridging chlorine atoms along the chain. The relationship between the chains, which are an $(\text{AABCCB})_n$ structure, is shown in Figure 14.⁹⁵ Such complexes have chain conductivities some six orders of magnitude greater than that of Wolfram's red salts with the same bridging halogen atom. The conductivity of $\text{K}_4[\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4\text{Cl}]\cdot 3\text{H}_2\text{O}$ is thermally activated, with a very low activation energy of $\sim 0.08 \text{ eV}$. The complexes crystallize as golden metallic needles in which the colours are largely determined by IVCT transitions in the $10\,000\text{--}20\,000 \text{ cm}^{-1}$ region.

The Raman spectrum of $\text{K}_4[\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4\text{Cl}]\cdot 3\text{H}_2\text{O}$ at resonance with the

⁹¹ C-M Che, W P Schaefer, H B Gray, M K Dickson, P Stein, and D M Roundhill, *J Am Chem Soc*, 1982, **104**, 4253

⁹² R J H Clark and M Kurmoo, *J Chem Soc, Dalton Trans*, 1985, 579

⁹³ M Kurmoo and R J H Clark, *Inorg Chem*, 1985, **24**, 4420

⁹⁴ R J H Clark, M Kurmoo, H M Dawes, and M B Hursthouse, *Inorg Chem*, 1986, **25**, 409

⁹⁵ L G Butler, M H Zietlow, C-M Che, W P Schaefer, S Sridhar, P J Grunthaner, B I Swanson, R J H Clark, and H B Gray, *J Am Chem Soc*, 1988, **110**, 1155

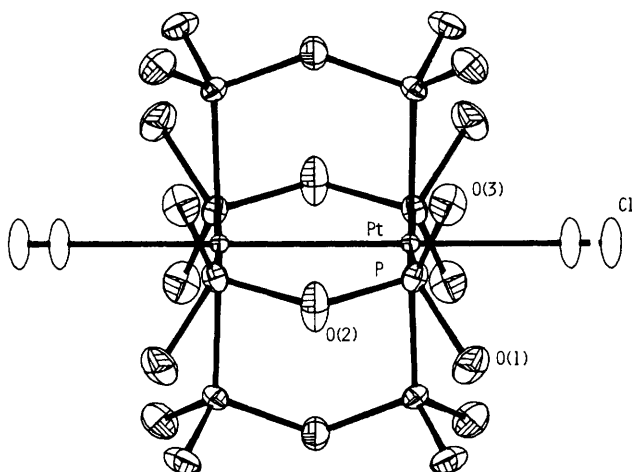


Figure 13 Model of the proposed chain repeat unit⁹⁴ in $K_4[Pt_2(H_2P_2O_5)_4Cl] \cdot 3H_2O$

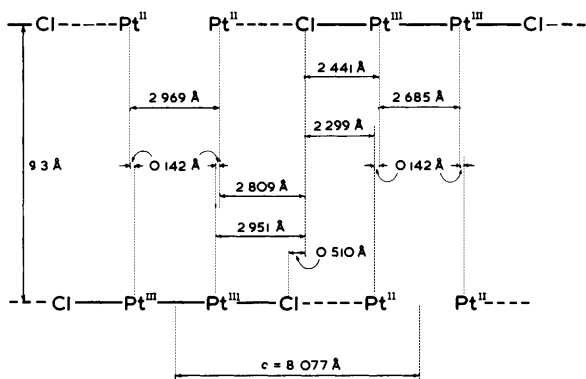


Figure 14 $(AABCCB)_n$ chain structure of $K_4[Pt_2(H_2P_2O_5)_4Cl] \cdot 3H_2O$ at 22 K

intervalence band is dominated by a band at 291 cm^{-1} ($\lambda_0 = 647.1 \text{ nm}$) which is assigned to the symmetric Pt—Cl stretching mode of the chain.⁹³ Its value is a little lower, on account of bridging, than that found (305 cm^{-1}) for the discrete diplatinum(III) species, $[Pt_2(H_2P_2O_5)_4Cl_2]^{4-}$. Six-membered progressions in the 291 cm^{-1} band are detected in the resonance Raman spectrum implying (a) that the chloride ion is not centrally bridging and (b) that the principal structural change undergone by the ion on excitation to the intervalence ($2\frac{1}{2}:2\frac{1}{2}$) oxidation state is—as for Wolfram's red complexes—substantial, and along the Pt—Cl coordinate. The close similarities between the PtPt and PtCl stretching frequencies of the isolated units and of the units as they occur in the chain suggest that the platinum ion valences approximate for this complex in the ground state to $\cdots II, II \cdots \cdots III, III \cdots$ (Table 3).

Table 3 Selected structural and vibrational data for diphosphite complexes platinum–platinum data

Complex	$r(\text{PtPt})/\text{\AA}$	$\nu(\text{PtPt})/\text{cm}^{-1}$	PtPt Bond Order	PtPt Oxidation State
$\text{K}_4[\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4] 2\text{H}_2\text{O}$	2 925	115	0	2,2
$\text{K}_4[\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4\text{Cl}] 3\text{H}_2\text{O}^a$	2 969	119	0	2,2
(22 K)	2 685	152	1	3,3
$\text{K}_4[\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4\text{Br}] 3\text{H}_2\text{O}^b$	2 781	117	0.5 – δ	2.5 – δ , 2.5 – δ
(19 K)		122	0.5 + δ	2.5 + δ , 2.5 + δ
$\text{K}_4[\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4\text{Cl}_2] 2\text{H}_2\text{O}$	2 695	158	1	3,3
$\text{K}_4[\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4\text{Br}_2] 2\text{H}_2\text{O}$	2 723	133	1	3,3

^a (AABCCB)_n structure ^b Symmetrically modified (AAB)_n structure

The X-ray crystallography of the analogous chain bromide was originally interpreted to imply that the bromine atom is centrally placed along the chain. This situation would be inconsistent with the expected Peierls distortion of a symmetric linear chain, and also with the observed Raman activity of $\nu(\text{PtX})$, though it would be consistent with relatively high chain conductivity.

However, neither the chain bromide nor the chain iodide yield progressions in $\nu(\text{PtX})$, as found for the chain chloride, at resonance with the intervalence band. This implies that the bridging atom is much nearer to the central position in these cases than is the case for the chain chloride, instead a progression in $\nu(\text{PtPt})$ is observed. Thus for the chain bromide or iodide, the platinum atoms are close to, but not exactly at, the +2.5 oxidation state. The results are summarized in Table 3, in which the oxidation states of the platinum atoms in $[\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4\text{Br}]^{4-}$ are represented as 2.5 – δ , 2.5 – δ , 2.5 + δ , 2.5 + δ , where δ might be as low as 0.1. These conclusions are in accord with those drawn on the basis of low temperature X-ray diffraction studies. These had, of necessity, to be carried out at 20 K in order for the thermal ellipsoids to be sufficiently small to demonstrate that the two equivalent positions of the bromine atoms were in fact 0.1 Å from the central position.⁹⁵

Much other work on further characterization of these complexes is in hand, particularly concerned with defining the nature of defect states in the chains and with investigating the consequences of applying pressures (4 GPa) to the complexes. The latter has the effect of reversing the Peierls transition, *i.e.* the complex reverts towards the symmetric linear chain,⁹⁶ as made evident by the red shift (750–1000 cm^{-1} per GPa) in the IVCT transition ($d_{\sigma}^2 \text{Pt}^{\text{II}}, \text{Pt}^{\text{II}} \longrightarrow d_{\sigma}^0 \text{Pt}^{\text{III}}, \text{Pt}^{\text{III}}$) (*cf.* for Wolfram's red, the red shift of the IVCT transition is 1600 cm^{-1} per GPa).

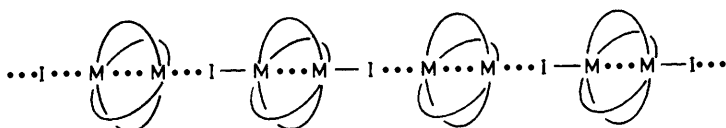
Much effort has also been applied towards the synthesis of analogous linear-

⁹⁶ B I Swanson, M A Stroud, S D Conradson, and M H Zietlow, *Solid State Commun.*, 1988 **65** 1405

chain complexes involving pcp rather than pop.⁹⁷ [pcp = HOP(O)CH₂P(O)OH, Figure 11.] However, complexes of this ligand have proved to be very difficult to isolate pure and in crystallographically characterizable form, although there is little doubt that chain complexes can be formed from the established [Pt₂(pcp)₄]⁴⁻ and [Pt₂(pcp)₄Cl₂]⁴⁻ moieties.⁹⁸

5 Dithioacetate Complexes

The diphosphite complexes described above are closely similar in both structures and properties to the dithioacetate complexes of platinum and nickel of the sort M₂(CH₃CS₂)₄I, M = Pt or Ni



These complexes are likewise semiconductors with essentially equal chain M–I bond distances (2.975 and 2.981 Å for M = Pt, 2.928 and 2.940 Å for M = Ni) and a Pt–Pt distance of 2.677 Å^{99,100} (which is about 0.1 Å shorter than in platinum metal). The complexes are thus close to being symmetrically bridged chains involving Pt^{2.5} alone. The ‘intervalence’ bands arising from interaction between the adjacent M₂(CH₃CS₂)₄ moieties occur in the 6000–8000 cm⁻¹ region with $\epsilon_{\max} \sim 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. The conductivity of a compressed powder of the material at 300 K is $7 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$, a value which is diminished from the true value by interparticle contact resistance and by averaging over all orientations. The temperature dependence of the conductivity (77–300 K) is such that the activation energy is only 0.05 eV ($\sim 400 \text{ cm}^{-1}$). The conductivity of a single crystal of Pt₂(CH₃CS₂)₄I at atmospheric pressure is $2 \Omega^{-1} \text{ cm}^{-1}$, a value which increases to $10 \Omega^{-1} \text{ cm}^{-1}$ at 7 GPa.¹⁰¹ Evaporated thin films ($\sim 500 \text{ \AA}$) of this complex have, moreover, been prepared *in vacuo* and found to possess a conductivity of $0.2 \Omega^{-1} \text{ cm}^{-1}$, a possibly significant finding for the electronics industry.¹⁰¹

Extensive infrared, Raman and resonance Raman studies of these and related sulphur-bonded complexes have recently been completed.^{102,103} The Raman spectra show strong resonance enhancement for excitation within the contours of the electronic bands in the visible region of the spectrum, but they have not yet been probed within the contour of the IVCT transition.

⁹⁷ R. J. H. Clark and C. M. Pout, unpublished work.

⁹⁸ C. King, R. A. Auerbach, F. R. Fronczek, and D. M. Roundhill, *Inorg. Chem.*, 1986, **108**, 5626.

⁹⁹ C. Bellito, A. Flamino, L. Gastaldi, and L. Scarramuzza, *Inorg. Chem.*, 1983, **22**, 444.

¹⁰⁰ C. Bellito, G. Dessy, and V. Fares, *Mol. Cryst. Liq. Cryst.*, 1985, **120**, 381; *Inorg. Chem.*, 1985, **24**, 2815.

¹⁰¹ I. Shirovani, Y. Inagaki, and M. Yamashita, ‘Physics and Chemistry of Organic Superconductors’, ISSP, 1989.

¹⁰² R. J. H. Clark and J. R. Walton, *Inorg. Chim. Acta*, 1987, **129**, 163.

¹⁰³ R. J. H. Clark and J. R. Walton, *J. Chem. Soc., Dalton Trans.*, 1987, 1535.

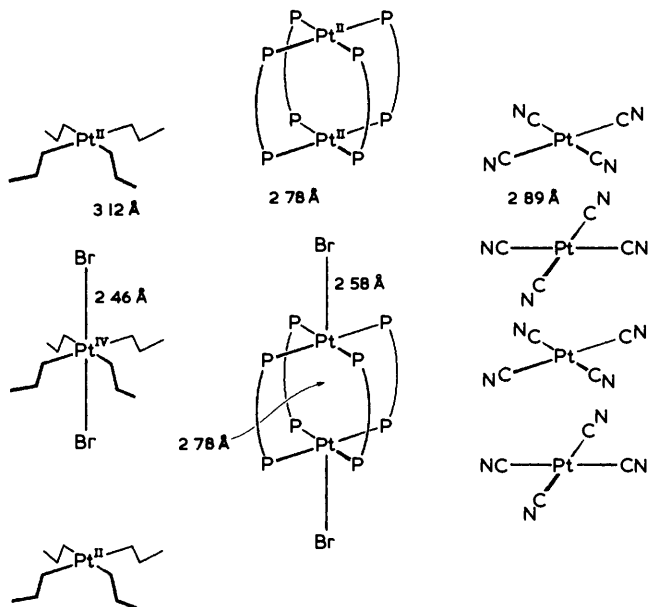


Figure 15 Structure of the chain of (from the left) *Rehlen's green* $[\text{Pt}(\text{C}_2\text{H}_5\text{NH}_2)_4]\text{Br}_2 \cdot 4\text{H}_2\text{O}$, $\text{K}_4[\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4\text{Br}] \cdot 3\text{H}_2\text{O}$, and $\text{KCP}, \text{K}_2\text{Pt}(\text{CN})_4 \text{Br}_{0.30} \cdot 3\text{H}_2\text{O}$

6 Conclusion

Both the degree of enhancement of the band assigned to ν_1 , the symmetric $\text{X}-\text{Pt}^{\text{IV}}-\text{X}$ stretch, as well as the length of the overtone progressions in ν_1 observed at resonance with the intervalence band of linear-chain complexes are related to the extent of structural change attendant upon excitation to the intervalence state. Spectacularly detailed band progressions are observed for these complexes, yielding an immense amount of valuable spectroscopic information. Of particular interest is the comparison of Wolfram's red type complexes with diphosphite complexes (Table 4). The latter have chain conductivities some 10^6 times greater than the former, and this can be understood to be a consequence of the more nearly central bridging of their chain chlorine or bromine atoms. In this context chain nickel complexes—especially those with central bridging halogen atoms—are potentially very important since they involve a cheaper metal and have comparatively high chain conductivities. It is, however, worth concluding by putting the chain conductivities of halogen-bridged complexes into perspective (Figure 15). The conductivity of KCP ($\sigma = 10^3 \Omega^{-1} \text{cm}^{-1}$) is 10^6 times greater than that of $\text{K}_4[\text{Pt}_2(\text{H}_2\text{P}_2\text{O}_5)_4\text{Br}] \cdot 3\text{H}_2\text{O}$ which, in

Table 4 Analogy between Wolfram's red salts and chain pop complexes: platinum-halogen (PtX) data (X = Cl or Br, etn = ethylamine)

	[Pt(etn) ₄][Pt(etn) ₄ X ₂]X ₄ ·4H ₂ O		K ₄ [Pt ₂ (H ₂ P ₂ O ₅) ₄ X]·3H ₂ O
$r(\text{PtCl})/\text{\AA}$	$\left. \begin{array}{l} 2.26 \\ 3.13 \end{array} \right\} 0.87$	$\left. \begin{array}{l} 2.37^a \\ 2.88 \end{array} \right\} 0.51$	$\left. \begin{array}{l} 2.299^b \\ 2.441 \end{array} \right\} 0.142$ $\left. \begin{array}{l} 2.809 \\ 2.951 \end{array} \right\} 0.142$
$\nu_1, \nu_{\text{sym}}(\text{PtCl})/\text{cm}^{-1}$	312.3 (to $\nu_1 = 16$ at res.)		291 (to $\nu_1 = 6$ at res.)
$r(\text{PtBr})/\text{\AA}$	$\left. \begin{array}{l} 2.46 \\ 3.12 \end{array} \right\} 0.66$	$\left. \begin{array}{l} 2.58 \\ 2.78 \end{array} \right\} 0.20$	
$\nu_1, \nu_{\text{sym}}(\text{PtBr})/\text{cm}^{-1}$	177.0 (to $\nu_1 = 11$ at res.)		210 223 (to $\nu_1 = 1$ only)

^{a,b} Assumes equivalent (a) or two different (b) PtPt bond lengths

turn, is a further 10^6 times greater than that of Reihlen's green (the bromo equivalent of Wolfram's red). All three complexes are bromides, but the first involves direct metal-metal bonds and short (2.89 Å) metal-metal distances. Those of the bromine-bridged species are much longer than this (5.36 and 5.58 Å, respectively) and this feature is clearly responsible for their much lower chain conductivities. In effect, the bridged complexes have easy access to lattice distortions which operate to generate band gaps and so prevent high conductivity.

The principal concern of this work has been to attempt to understand the relationships between structure, spectroscopy, conductivity, and bonding in chain complexes likely to be of interest as new materials with desirable properties.

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