

TILDEN LECTURE*

The Chemistry and Spectroscopy of Mixed-valence Complexes

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1 Introduction

The considerable current interest in the bonding in, and properties of, mixed-valence complexes, well discussed at a recent NATO ASI¹ and elsewhere,²⁻⁵ derives from the importance of such materials in fields as diverse as solid-state physics, inorganic chemistry, materials science, geology, and bioinorganic chemistry. At least 40 elements in the periodic table form mixed-valence species, and the importance of these species stems as much from their rich and varied chemistry as from their unexpectedly wide range of physical properties. On the geological side many minerals contain an element such as iron in two different oxidation states (*e.g.* magnetite Fe_3O_4 , biotite $\text{KH}_2(\text{Mg,Fe})_3\text{Al}(\text{SiO}_4)_3$, vivianite $\text{Fe}_3\text{P}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$) and this has structural, magnetic, and electronic consequences. On the bioinorganic side, the electron-transport properties of certain metalloporphyrin and mixed-valence iron-sulphur cluster systems are known to be important in biological processes. The subject of mixed-valence chemistry is now so far-reaching that it deserves substantial treatment in its own right in standard textbooks of Inorganic Chemistry.

Although there are many intriguing properties of mixed-valence complexes, it is usually their colours which are their most striking feature. Indeed, this has been recognized industrially since at least the early 18th century⁶ when Prussian blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot 14\text{H}_2\text{O}$ (Figure 1) began to be manufactured as a dyestuff. This complex owes its deep blue colour ($\tilde{\nu}_{\text{max.}} = 14\,100\text{ cm}^{-1}$, $\epsilon_{\text{max.}} = 10^4\text{ M}^{-1}\text{ cm}^{-1}$)⁷ not to ligand-field transitions, or to charge-transfer transitions of the

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¹ 'Mixed-valence Compounds', ed. D. B. Brown, Proc. NATO ASI, Oxford, Sept. 1979; Reidel, Dordrecht, 1980.

² 'Chemistry and Physics of One-Dimensional Metals' ed. H. J. Keller, Plenum, New York, 1977.

³ 'Synthesis and Properties of Low-Dimensional Materials', J. S. Miller and A. J. Epstein, *Ann. N.Y. Acad. Sci.*, 1978, **313**, 1-828.

⁴ 'Molecular Metals', ed. W. E. Hatfield, Plenum, New York, 1979.

⁵ 'Extended Linear Chain Compounds', ed. J. S. Miller, Plenum, New York, Vols. 1 and 2, 1982; Vol. 3, 1983.

⁶ 'Miscellanea Berolinensia ad incrementum scientiarum', Berlin, 1710, p. 377.

⁷ H. J. Buser, D. Schwarzenbach, W. Petter, and A. Ludi, *Inorg. Chem.*, 1977, **16**, 2704.

sort ligand \rightarrow metal, metal \rightarrow ligand, or ligand \rightarrow ligand, but to an intervalence transition of the sort $\text{Fe}^{\text{II}} \rightarrow \text{Fe}^{\text{III}}$. Such transitions are often strongly allowed, in which case they dominate the spectrum and thus (if in the visible region) are responsible for the colour of the material.

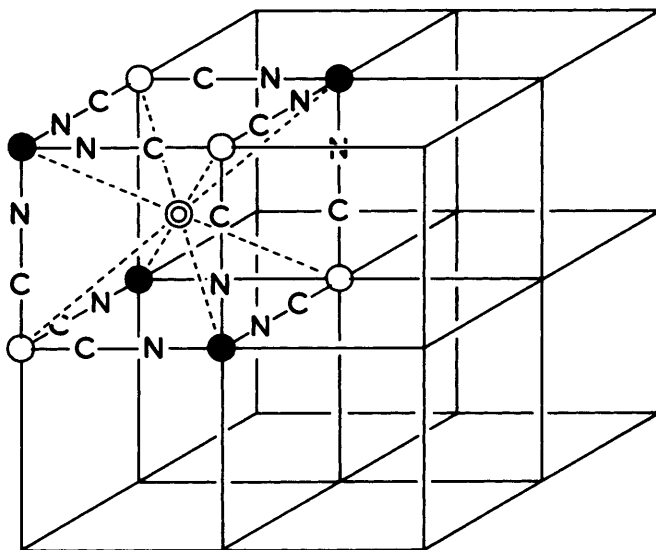


Figure 1 The unit cell of Prussian Blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot 14\text{H}_2\text{O}$ $\circ = \text{Fe}^{\text{II}}$, $\bullet = \text{Fe}^{\text{III}}$

The other striking and, at first sight, unexpected property of certain mixed-valence complexes is their electrical conductance. Both 'controlled-valence-semiconductors' such as $\text{Li}_x\text{Ni}_{1-x}\text{O}$ ($0 < x < 1$), with a conductance of 10^{10} times that of NiO , and one-dimensional conductors such as $\text{K}_2\text{Pt}(\text{CN})_4 \cdot \text{Br}_{0.30} \cdot 3\text{H}_2\text{O}$ (KCP), with a conductance of $\sim 10^9$ times that of $\text{K}_2\text{Pt}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$ (Table 1), display properties vastly different from those of their parent single-valence constituents. These features constitute sufficient reason for carrying out concerted studies of a wide range of mixed-valence materials. However, although many extended-chain structures are potential one-dimensional conductors, their propensity towards bond alternation prevents this possibility from being fully realised. A recent analysis of the question of bond alternation in one-dimensional polymers has led to the conclusion⁸ that this feature can be largely circumvented by the appropriate design of off-axis acceptor ligands and of bridging ligands with high ligand-ligand repulsion.

The basis of the static model for the classification of mixed-valence complexes

⁸ S. Shaik and R. Bar, *Inorg. Chem.*, 1983, **22**, 735.

Table 1 Properties of chain platinum species^a

Species	$\sigma_{\parallel}(298 \text{ K})/\Omega^{-1} \text{ cm}^{-1}$	Colour	$r(\text{Pt-Pt})/\text{\AA}$
$\text{K}_2[\text{Pt}(\text{CN})_4]\cdot 3\text{H}_2\text{O}$	5×10^{-7}	white	3.48
$\text{K}_2[\text{Pt}(\text{CN})_4]\text{Br}_{0.30}\cdot 3\text{H}_2\text{O}$	3×10^2	copper	2.89
Pt metal	9.4×10^4	silver	2.77

^a Ref. 17.

was laid down in 1967 by Robin and Day and by Hush.⁹⁻¹¹ In short, the basis relates to the degree to which the sites occupied by elements of different valence can be distinguished in their ground state and the ease or difficulty with which an electron can be transferred from one site (A) to another (B). Class I complexes are those in which the A and B sites are very different from one another, and thus are ones in which the valences are firmly localized (trapped-valence species). The properties of such complexes are, to a good approximation, the sums of the properties of the constituent ions. They are insulators ($\sigma < 10^{-12} \Omega^{-1} \text{ cm}^{-1}$ at room temperature and atmospheric pressure), and any intervalence transitions $\text{A}^n\text{B}^{n+1} \rightarrow \text{A}^{n+1}\text{B}^n$ occur at such large energies as to lie well into the ultraviolet region. Accordingly, such complexes are of no particular spectroscopic interest.

Class II complexes are ones in which the A and B sites are more similar to one another than is the case for class I complexes, but nevertheless ones in which the sites are distinguishable crystallographically. The valences, although localized, can exchange with a relatively small expenditure of energy. Thus intervalence transitions may, and indeed do, occur in the visible region of the spectrum, sometimes with considerable oscillator strengths. Many complexes in this category form as linear chains, the prototype being Wolfram's Red, $[\text{Pt}(\text{etn})_4][\text{Pt}(\text{etn})_4\text{Cl}_2]\cdot \text{Cl}_4\cdot 4\text{H}_2\text{O}$ (etn = ethylamine), a complex involving platinum in the (formal) oxidation states II and IV (Figure 2). Such materials have conductances in the axial (chain) direction in the ranges found for insulators to semiconductors ($\sigma_{\parallel} \sim 10^{-12} - 10^{-8} \Omega^{-1} \text{ cm}^{-1}$). The conductance is highly anisotropic ($\sigma_{\parallel}/\sigma_{\perp} \sim 300$) and very pressure sensitive (σ_{\parallel} increases by *ca.* 10^9 on increasing the pressure to 130 kbar).¹²

Class III (delocalized valence) complexes are ones in which the A and B sites are indistinguishable and the key element has a non-integral oxidation state. This class is usually divided into two, the class IIIA and IIIB sub-divisions. In the former, the delocalization of the valence electrons is considered (in the first instance on structural grounds) to take place only within a cluster of equivalent metal ions. No individual ion properties can be distinguished, and it is debatable whether or not the low-lying electronic transitions of such species should reason-

⁹ 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.

¹⁰ N. S. Hush, in 'Progress in Inorganic Chemistry', ed. F. A. Cotton, Wiley, New York, Vol. 8, 1967, pp. 357 and 391.

¹¹ P. Day in 'International Reviews in Physical Chemistry', Butterworths, London, Vol. 1, 1981, p. 149.

¹² L. V. Interrante, K. W. Browall, and F. B. Bundy, *Inorg. Chem.*, 1974, 13, 1158.

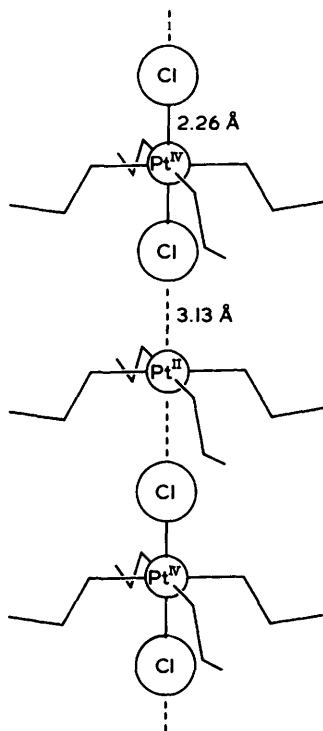


Figure 2 Structure of Wolffram's Red, $[\text{Pt}(\text{etn})_4][\text{Pt}(\text{etn})_4\text{Cl}_2]\text{Cl}_4 \cdot 4\text{H}_2\text{O}$, where etn = ethylamine

ably be termed intervalence transitions. The bonding in such complexes is probably best treated on a molecular orbital basis, and the allowed transitions as $\pi \rightarrow \pi^*$ transitions, *etc.*, of the cluster as a whole. A typical example would be the cubic $[\text{Nb}_6\text{Cl}_{12}]^{2+}$ ion, which involves equivalent metal ions each in the +2.33 oxidation state (Figure 3).

Class IIIB complexes are delocalized valence ones in which the lattice is continuous. Again, no properties characteristic of the constituent ions can be distinguished. Indeed, many such materials not only have a coppery bronze appearance and strikingly reflect visible light, but behave as metallic conductors (*e.g.* KCP, Figure 4 and Table 1). The bonding in such complexes is best treated by band theory.^{13,14}

Representative examples of the very large number of known mixed-valence complexes are given in Table 2. Not included in the table, however, are the

¹³ M.-H. Whangbo and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 6093.

¹⁴ M.-H. Whangbo, *Acc. Chem. Res.*, 1983, **16**, 95.

significant number of complexes, *e.g.* the Creutz-Taube ion,¹⁵ $[(\text{NH}_3)_5\text{Ru}(\text{pyrazine})\text{Ru}(\text{NH}_3)_5]^{5+}$, which apparently lie near to the class II/III borderline and which are therefore subject to considerable speculation as to their correct classification.

The main features of interest in the rich and varied chemistry of mixed-valence complexes are the relationships between gross physical properties, (*e.g.* colour, electrical conductance), molecular structure, and the extent of valence-electron delocalization. Indeed, a great many physical techniques have been used in the course of defining the last, and hence the class to which a mixed-valence species belongs. Our spectroscopic interest centres around^{16,17} (*a*) the wavenumbers, intensities, bandwidths, and assignments of the intervalence transitions, (*b*) the behaviour of Raman bands of mixed-valence species both on and off resonance with intervalence transitions and (*c*) the nature of the geometric changes undergone by such complexes on excitation to the intervalence state. Information on point (*c*) derives from the fact that, if there is a change in geometry of a molecule on transition from the ground to an excited state, then the normal co-ordinate responsible for effecting this structural change is found to give rise to a Raman band that is much enhanced (relative to its intensity in the off-resonance situation) when the exciting line wavenumber coincides with that of the electronic transition in question.¹⁸

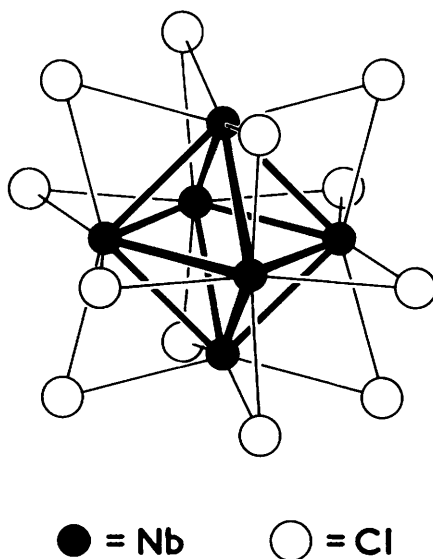


Figure 3 Structure of $[\text{Nb}_6\text{Cl}_{12}]^{2+}$

¹⁵ C. Creutz and H. Taube, *J. Am. Chem. Soc.*, 1969, **91**, 3988.

¹⁶ R. J. H. Clark, Ref. 1, p. 271; *J. Mol. Struct.*, 1984, **113**, 117.

¹⁷ 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.

¹⁸ Y. Nishimura, A. Y. Hirakawa, and M. Tsuboi, in 'Advances in Infrared and Raman Spectroscopy', ed. R. J. H. Clark and R. E. Hester, Heyden, London, Vol. 5, 1978, p. 217.

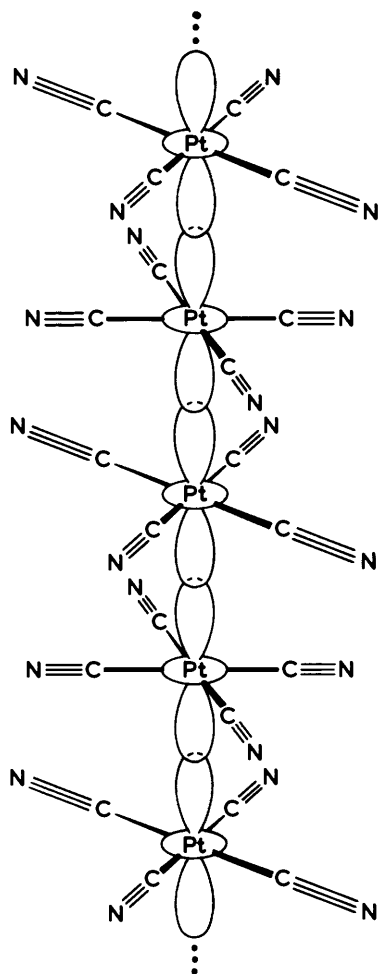


Figure 4 Structure of KCP, $K_2Pt(CN)_4 \cdot Br_{0.30} \cdot 3H_2O$

Also of importance is the connection between the physical properties of mixed-valence compounds and the rates of electron-transfer reactions in solution. The key prediction as far as mechanistic inorganic chemists are concerned is that moderately coupled mixed-valence compounds should possess an intervalence band at an energy, E_{op} , which is (for one-electron transfer processes) simply related to the barrier for thermal electron-transfer, E_{th} . For symmetric species,

$$E_{op} = 4 E_{th}$$

Further, the full width at half maximum ($\Delta\tilde{\nu}_{1/2}$) of the intervalence band should be a

Table 2 Examples of different classes of mixed-valence compound^a

Class	Example	Site A Geometry	Formal Oxidation State	Site B Geometry	Formal Oxidation State
I	[Co(NH ₃) ₆] ₂ [CoCl ₄] ₃	Tetrahedral (high spin)	II	Octahedral (low spin)	III
	[Cu(en) ₂][CuBr ₂] ₂ ^b	Linear	I	Square planar	II
	Ga[GaCl ₄] (≡ 'GaCl ₂ ') Ga-Cl = 3.2–3.3 Å	Dodecahedral (distorted)	I	Tetrahedral	III
II	[Au(dmg) ₂][AuCl ₂] ^c	Linear	I	Square planar	III
	Fe ₄ [Fe(CN) ₆] ₃ ·14H ₂ O Fe-C = 1.92 Å	Octahedral	II	Octahedral	III
	[Pt(etn) ₄][Pt(etn) ₄ Cl ₂] Cl ₄ ·4H ₂ O ^d	Square planar/ axially distorted octahedral (linear chain complex)	II	Octahedral	IV
IIIA	[NH ₄] ₂ [SbBr ₆] Sb-Br = 2.79 Å	Octahedral	III	Octahedral	V
	[Mo Mo ₅ O ₁₉] ³⁻	Octahedral	V	Octahedral	VI
	[Nb ₆ Cl ₁₂]Cl ₂	4:4:1 Co-ordination	2.33		
	[Fe ₄ S ₄ (SCH ₂ Ph) ₄] ²⁻	Tetrahedral	2.5		
	[(NH ₃) ₅ OsN ₂ Os(NH ₃) ₅] ⁵⁺	Octahedral	2.5		
	[Tc ₂ Cl ₈] ³⁻	Square pyramidal	2.5		
IIIB	S ₄ ²⁺	Square planar	0.5		
	[(PEt ₂ Ph) ₃ RuCl ₃ Ru- (PEt ₂ Ph) ₃] ²⁺	Pseudo-octahedral	2.5		
	K _{1.75} Pt(CN) ₄ ·1.5H ₂ O Pt-Pt = 2.96 Å	Square planar (linear chain complex,	2.25		
	K ₂ Pt(CN) ₄ ·Br _{0.30} ·3H ₂ O Pt-Pt = 2.89 Å	Square planar (linear chain complex,	2.30		
	Hg _{2.86} AsF ₆	Linear	0.35		
Na _x TiO ₂ (0 < x < 1)	Octahedral	(III–IV)			
Na _x WO ₃ (0.4 < x < 0.9)	Octahedral	(V–VI)			

^a Site A is arbitrarily taken to be the one in which the metal ion has the lower valence. ^b en = 1,2-diaminoethane. ^c dmg = dimethylglyoxime. ^d etn = ethylamine.

function of the wavenumber of its maximum absorption, $\tilde{\nu}_{\max}$, which in turn should be a function of the dielectric constant of the solvent. Since 1969, a great many substitution-inert dinuclear complexes related to the Creutz-Taube ion have been synthesized in order to probe the energetics of electron-transfer processes in solution and the mechanisms and magnitudes of electronic interactions between metal centres. This aspect of mixed-valence chemistry will not be developed here since it has been reviewed recently elsewhere.^{11,19,20} The important result, in the

¹⁹ R. D. Cannon, in 'Advances in Inorganic Chemistry and Radiochemistry', ed. H. J. Emeléus and A. G. Sharpe, Academic Press, Vol. 21, 1978, p. 179.

²⁰ C. Creutz, in 'Progress in Inorganic Chemistry', ed. S. J. Lippard, Wiley, Vol. 30, 1983, p. 1.

context of the present article, is that class II mixed-valence species undergo light absorption at an energy related to E_{th} , whereas class III species do so at an energy $h\nu = 2H_{\text{AB}}$, where H_{AB} is the resonance electronic coupling energy between centres A and B.

2 Class II Linear-chain Complexes

Since the properties of class I complexes are simply the sums of the properties of the component species, there is little if any new information to be learned from spectroscopic studies of such materials. By contrast, the spectroscopy of class II complexes is rich and varied, particularly that relating to halogen-bridged linear-chain complexes. Extensive electronic, infrared, Raman and resonance Raman studies of platinum and, to a much lesser extent, palladium complexes of this sort have yielded a very large amount of intriguing spectroscopic information thereon.

The chloro-complexes of this sort may be prepared in a variety of ways, most notably by (a) reaction of equimolar amounts of the platinum(II) and platinum(IV) constituents in a suitable solvent or (b) partial oxidation of the constituent platinum(II) species with an oxidizing agent such as chlorine, ammonium persulphate, hydrogen peroxide, or copper(II) halide. The exact experimental details appropriate to optimum yield and purity are different in each case. The analogous bromo- and iodo-species may be prepared in a similar manner, or from the chloro-species by halogen exchange with, for example, HBr or HI. Such complexes all have the same basic structures (Figure 2), involving five different charge types (Table 3) and in which the equatorial ligand (L) is an amine such as NH_3 or EtNH_2 and $\text{X} = \text{Cl}, \text{Br}, \text{or I}$. Bidentate ligands $\widehat{\text{LL}}$ can also form complexes of this sort, where $\widehat{\text{LL}}$ represents (for instance) 1,2-diaminoethane, 1,2-diaminopropane, 1,3-diaminopropane, 1,2-diaminobutane, 1,2-diaminocyclopentane, or 1,2-diaminocyclohexane. (Note, however, that not all possible combinations of L and X are known to yield isolable complexes.) There are also examples where $\widehat{\text{LL}}\widehat{\text{L}}$ represents the terdentate ligand diethylenetriamine (dien), *viz.* $[\text{Pt}^{\text{II}}(\text{dien})\text{I}]$ -

Table 3 *Halogen-bridged mixed-valence complexes of platinum*

Charge per Pt unit	Examples ^a
+2	$[\text{Pt}^{\text{II}}(\text{etn})_4][\text{Pt}^{\text{IV}}(\text{etn})_4\text{Cl}_2]\text{Cl}_4 \cdot 4\text{H}_2\text{O}$ $[\text{Pt}^{\text{II}}(\text{en})_2][\text{Pt}^{\text{IV}}(\text{en})_2\text{Br}_2][\text{ClO}_4]_4$
+1	$[\text{Pt}^{\text{II}}(\text{dien})\text{I}][\text{Pt}^{\text{IV}}(\text{dien})\text{I}_3]\text{I}_2$
0	$[\text{Pt}^{\text{II}}(\text{NH}_3)_2\text{Cl}_2][\text{Pt}^{\text{IV}}(\text{NH}_3)_2\text{Cl}_4]$ $[\text{Pt}^{\text{II}}(\text{en})\text{Cl}_2][\text{Pt}^{\text{IV}}(\text{en})\text{Cl}_4]$
-1	$\text{K}_2[\text{Pt}^{\text{II}}(\text{NH}_3)\text{Cl}_3][\text{Pt}^{\text{IV}}(\text{NH}_3)\text{Cl}_5] \cdot 2\text{H}_2\text{O}$ $\text{Cs}_2[\text{Pt}^{\text{II}}(\text{NO}_2)(\text{NH}_3)\text{I}_2][\text{Pt}^{\text{IV}}(\text{NO}_2)(\text{NH}_3)\text{I}_4]$
-2	$\text{K}_4[\text{Pt}^{\text{II}}\text{I}_4][\text{Pt}^{\text{IV}}\text{I}_6]$

^a etn = ethylamine, dien = diethylenetriamine, en = 1,2-diaminoethane.

$[\text{Pt}^{\text{IV}}(\text{dien})\text{I}_3]\text{I}_2^{21}$ and, in the case of palladium, where $\text{\textcircled{LLLL}}$ represents the tetradentate macrocyclic ligand 1,4,8,11-tetra-aza-cyclotetradecane (cyclam), *viz.* $[\text{Pd}^{\text{II}}(\text{cyclam})][\text{Pd}^{\text{IV}}(\text{cyclam})\text{X}_2]\text{Y}_4$, where $\text{X} = \text{Cl}$ or Br .²² Typical counteranions are K^+ , Cs^+ , or NH_4^+ and counter-anions are Cl^- , Br^- , I^- , $[\text{HSO}_4]^-$, $[\text{ClO}_4]^-$, $[\text{BF}_4]^-$, $[\text{NO}_3]^-$, as well as polymeric copper halide chains such as $[\text{CuX}_4]^{3-}$ ($\text{X} = \text{Cl}$ or Br) and $[\text{Cu}_3\text{Br}_5]^{2-}$. This type of complex can be regarded as the archetypal class II or localized valence complex in which the two metal atoms differ in oxidation state by two, just as Prussian Blue is so regarded for those complexes in which the two metal atoms differ in oxidation state by one.

The extent of valence-electron delocalization is considered to increase as the bridging atom changes in the order $\text{Cl} < \text{Br} < \text{I}$. One pointer to this is that, from the large amount of *X*-ray structural work carried out on these complexes (summarized in ref. 17), the $r(\text{Pt}^{\text{IV}}\text{-X})/r(\text{Pt}^{\text{II}}\text{-X})$ ratio increases in the order of $\text{Cl} < \text{Br} < \text{I}$ [the average values being 0.75 (chlorides), 0.79 (bromides), 0.88 (iodides)]. This has the consequence that the iodine-bridged species have the highest chain conductance and intervalence bands of the lowest energies (*vide infra*).

A curious structural feature of these complexes, (not shared by other class II species such as Prussian Blue) is that, although the two metal-atom sites are structurally distinguishable, they may be interconverted by a concerted movement of the axial halogen atoms in phase, away from platinum(IV) towards platinum(II), *i.e.* the distinction between platinum(II) and platinum(IV) is defined only by the position of the bridging atom. The interconversion could be brought about, for instance, by consecutive one-electron jumps $\text{Pt}^{\text{II}} \rightarrow \text{Pt}^{\text{IV}}$ *via* the intermediacy of the $\text{Pt}^{\text{III}}\text{-Pt}^{\text{III}}$ state. The ease with which such a transition takes place is connected with the one-dimensional insulator/semi-conductor nature of the complexes. Moreover the electrical conductance in the axial direction is *ca.* 300-times greater than that in the perpendicular directions.¹² The property of interconversion of oxidation states through a symmetrical intermediate is a feature of certain other mixed-valence systems, *viz.* $\text{Sb}^{\text{III,V}}$ and $\text{Pb}^{\text{II,IV}}$ hexahalides, *etc.*

The $\text{Pt}^{\text{II}} \rightarrow \text{Pt}^{\text{IV}}$ intervalence transitions, as judged by transmission spectral measurements, occur in the region 25 000—18 200 cm^{-1} for chloro-bridged species, 23 600—14 300 cm^{-1} for bromo-bridged species, and 20 600—7 500 cm^{-1} for iodo-bridged species, the trend $\text{Cl} > \text{Br} > \text{I}$ being consistent with the reverse trend for the electrical conductances of such complexes. The transition energies for materials that have strong absorbance and high reflectivity are difficult to determine unless single-crystal specular reflectance measurements are carried out. In this case Kramer's-Kronig analysis of the data leads to plots of the real (ϵ') and imaginary (ϵ'') parts of the dielectric constant as a function of wavenumber, these quantities being related to the transition energy or gap frequency of a semi-conductor. Alternatively, and more easily, the transition energy can be related to the excitation profile of a resonance-enhanced Raman band of the complex (*i.e.* a

²¹ R. J. H. Clark, M. Kurmoo, A. M. R. Galas, and M. B. Hursthouse, *J. Chem. Soc. Dalton Trans.*, 1983, 1583.

²² M. Yamashita, H. Ito, K. Toriumi, and T. Ito, *Inorg. Chem.*, 1983, **22**, 1566.

plot of Raman band intensity versus excitation line wavenumber).²³⁻²⁵

The wavenumber of the intervalence transition is related to the $\text{Pt}^{\text{II}} \cdots \text{Pt}^{\text{IV}}$ chain distance, as evident from Figure 5 which pertains to the results of a large number of spectroscopic and crystallographic studies on such complexes.¹⁷ It is interesting that an extrapolation of the plots for chlorides and bromides crosses the zero for the intervalence transition energy at *ca.* 4.6 and 4.8 Å, respectively. These values correspond approximately to twice the $r(\text{Pt}^{\text{IV}}\text{-Cl})$ and $r(\text{Pt}^{\text{IV}}\text{-Br})$ distances, respectively, *i.e.* to the situation in which the bridging halogen atom is centrally placed between the metal atoms. The slightly erratic nature of the relationship is due to the fact that the intervalence transition energy also depends on the $r(\text{Pt}^{\text{IV}}\text{-X})/r(\text{Pt}^{\text{II}}\text{-X})$ ratio, which in turn depends on the extent of hydrogen-bonding between the amines and the counterions. This will vary widely, from zero for neutral chain complexes to very significant values for $[\text{Pt}(\text{NH}_3)_4][\text{Pt}(\text{NH}_3)_4\text{I}_2]\cdot[\text{HSO}_4]_3[\text{OH}]\cdot\text{H}_2\text{O}$, in which one of the $r(\text{N} \cdots \text{O})$ distances is as little as 2.79 Å.¹⁷

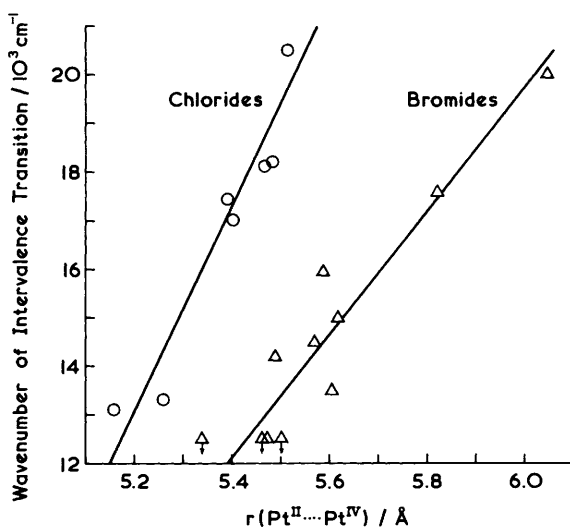


Figure 5 Relationship between the intervalence transition wavenumber (as deduced from the maxima in the ν_1 band excitation profiles) for linear-chain halogen-bridged platinum complexes and the $\text{Pt}^{\text{II}} \cdots \text{Pt}^{\text{IV}}$ chain distance

The Raman spectra of halogen-bridged mixed-valence complexes of platinum, obtained with an exciting line resonant with the $\text{Pt}^{\text{II}} \rightarrow \text{Pt}^{\text{IV}}$ intervalence band, are characterized by an enormous intensification to the Raman band attributed to the symmetric stretching mode, $\nu_1(\text{X-Pt}^{\text{IV}}\text{-X})$ of the chain-halogen atoms, together with the development of an intense overtone progression $\nu_1\nu_1$, where ν_1 is the

²³ G. C. Papavassiliou and A. D. Zdetsis, *J. Chem. Soc., Faraday Trans. 2*, 1980, 104.

²⁴ G. C. Papavassiliou and C. S. Jacobsen, *J. Chem. Soc., Faraday Trans. 2*, 1981, 191.

²⁵ R. J. H. Clark and M. Kurmoo, *J. Chem. Soc., Dalton Trans.*, 1983, 761.

vibrational quantum number of this mode. As many as 17 harmonics of the ν_1 mode have given rise to detectable bands in the resonance Raman spectra of some complexes of this sort. Much weaker, subsidiary progressions also appear in many cases, these mainly consisting of progressions in ν_1 based upon one quantum of another Raman-active mode. The resonance Raman spectrum of Wolfram's Red (Figure 6), which is typical, clearly indicates the dominant features of the $\nu_1\nu_1$ progression ($\nu_1 \sim 310 \text{ cm}^{-1}$).

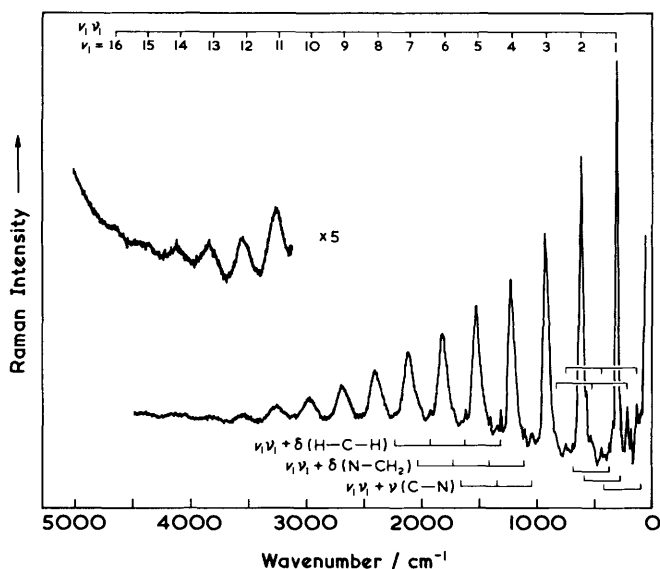


Figure 6 Resonance Raman spectrum of Wolfram's Red $[\text{Pt}(\text{etn})_4][\text{Pt}(\text{etn})_4\text{Cl}_2]\text{Cl}_4 \cdot 4\text{H}_2\text{O}$ at ca. 80 K using an exciting line of wavelength 514.5 nm

A vast amount of spectroscopic information on complexes of this sort has now been gathered and reviewed.¹⁷ From such data it is possible, by standard procedures,²⁶ to calculate approximate values for the harmonic wavenumbers (ω_1) and anharmonicity constants (x_{11}). Cross terms (x_{ij}) may also be determined if subsidiary progressions are observed in the spectra. The average values of ω_1 for a wide variety of bridged complexes are given in Table 4, from which it is clear that, for any given halide, ω_1 falls slightly in the order cation chain > neutral chain > anion chain. The average Pt-X bond lengths increase slightly in this same order, *cf.* the well known reciprocal relationship between bond lengths and bond stretching frequencies.²⁷

The known x_{11} values, which average -0.98 , -0.41 , and -0.25 cm^{-1} for chlorides, bromides, and iodides, respectively, are about an order of magnitude

²⁶ R. J. H. Clark and B. Stewart, *Struct. Bonding (Berlin)*, 1979, **36**, 1.

²⁷ R. J. H. Clark, *Spectrochim. Acta*, 1965, **21**, 955.

Table 4 Average values for ω_1/cm^{-1} for different types of linear-chain mixed-valence complex of platinum^a

Bridging group	Charge type		
	Cationic	Neutral	Anionic
Cl	309.1	307.8	297.8
Br	175.7	168.6	172.0
I	122.3	120.8	114.2

^a Ref 17

larger than those found for typical single-valent molecular species such as group IV tetrahalides.^{28,29} Nevertheless, they are not large and, curiously, plots of $v_1 v_1/v_1$ versus v_1 remain linear even out as far as $17v_1$. Although $17v_1$ occurs at ca. 5 000 cm^{-1} up the potential energy curve, it must nevertheless lie below the expected crossing points between the potential energy curves for (II,IV), (III,III), and (IV,II) (Figure 7). leading to no deviations from linearity for the higher harmonics. Presumably, owing to the rather low oscillator strengths ($f \sim 10^{-4}$)^{30,31} of the intervalence transitions for linear-chain platinum complexes (high chromophore concentrations in the complexes is responsible for their deep colours rather than high oscillator strengths) the extent of interaction between the different potential energy curves is slight, and they remain nearly parabolic even far from their minima. Note that the position of the minimum in the (III,III) curve relative to the cross-over point between the (II,IV) and (IV,II) points is uncertain.

The implication of the long overtone progression observed in the Raman spectrum of such complexes at resonance with the intervalence transition is that the $\text{Pt}^{\text{IV}}\text{-X}$ bond lengths must extend very substantially on excitation from the ground to the resonant excited state.

It is possible, by way of the theories of Mingardi and Siebrand³² and Clark and Stewart,³³ to calculate the magnitudes of these bond-length changes on excitation, but usually only for those species for which the resonant electronic transition is vibronically structured. This is not the case here unfortunately, even at liquid helium temperature.³⁰ However, by analogy with the results for species which do have structured resonant bands, *viz.* MnO_4^- , MoS_4^{2-} , WS_4^{2-} ,³³⁻³⁶ the $\text{Pt}^{\text{IV}}\text{-Cl}$ bond length increases in the intervalence state by probably 0.1—0.2 Å. Such a large

²⁸ R. J. H. Clark and P. D. Mitchell, *J. Am. Chem. Soc.*, 1973, **95**, 8300.

²⁹ R. J. H. Clark and T. J. Dines, *Inorg. Chem.*, 1980, **19**, 1681.

³⁰ H. Tanino, J. Nakahara, and K. Kobayashi, *J. Phys. Soc. Jpn.*, 1980, **49**, Suppl.A, 695.

³¹ R. Aoki, Y. Hamaue, S. Kida, M. Yamashita, T. Takemura, Y. Furuta, and A. Kawamori, *Mol. Cryst. Liq. Cryst.*, 1982, **81**, 301.

³² M. Mingardi and W. Siebrand, *J. Chem. Phys.*, 1975, **62**, 1074.

³³ R. J. H. Clark and B. Stewart, *J. Am. Chem. Soc.*, 1981, **103**, 6593.

³⁴ R. J. H. Clark, T. J. Dines, and M. L. Wolf, *J. Chem. Soc., Faraday Trans. 2*, 1982, **78**, 679.

³⁵ R. J. H. Clark, T. J. Dines, and G. P. Proud, *J. Chem. Soc., Dalton Trans.*, 1983, 2019.

³⁶ R. J. H. Clark, *Adv. Chem. Ser.*, 1983, **211**, 509.

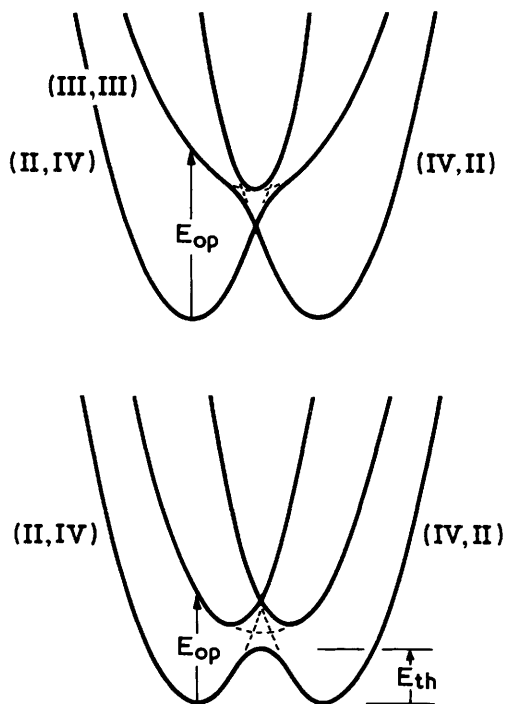


Figure 7 Potential energy surfaces for the (II,IV) and (IV,II) states of a linear-chain platinum complex, showing the optical (Franck-Condon) intervalence transitions (E_{op}). Note (a) that the (II,IV) and (IV,II) surfaces do not interact in first order, owing to the fact that direct interconversion corresponds to a two-electron jump and (b) that the position of the minimum in the (III,III) curve relative to the cross-over point between the (II,IV) and (IV,II) curves is not known. The dashed lines indicate 'non-crossing' regions

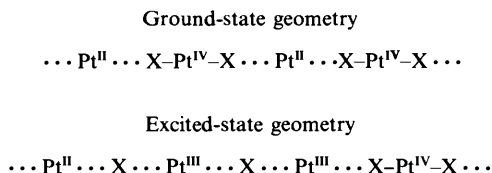


Figure 8 Geometric distortion of linear-chain complexes on excitation to the intervalence state

bond-length change is consistent with the various proposed processes (Figure 8) for the axial conductivity of such materials. This structural change is just that expected on excitation to the (III,III) state since, in its relaxed excited-state geometry, the axial halogen atom would have no reason to be other than centrally placed between the two platinum atoms. Consistent with all these results, the large amount of crystallographic data on these complexes¹⁷ reveals that the halogen would need to

move 0.1—0.4 Å in the chain direction in order to reach the central position between the metal atoms.

It is rare that subsidiary progressions in ν_1 , based on one or more quanta of another Raman-active mode, have much intensity, consistent with the resonant transition being z -polarized and localized in the chain direction. However, in the case of the complexes $\text{Cs}_2[\text{Pt}(\text{NO}_2)(\text{NH}_3)\text{X}_2][\text{Pt}(\text{NO}_2)(\text{NH}_3)\text{X}_4]$, $\text{X} = \text{Br}$ or I , some equatorial modes do give rise to Raman bands enhanced at resonance with the intervalence band.³⁷ Specifically, the resonance Raman spectrum of the bromo-complex consists of eleven progressions of three or more members, in nine of which ν_1 acts as the progression-forming mode. In some of these progressions the equatorial mode ν_2 , the symmetric $\text{Br}-\text{Pt}^{\text{IV}}-\text{Br}$ stretching mode of the trans-equatorial bromides, and $\nu(\text{NO}_2)_s$ and $\delta(\text{NO}_2)_s$, the symmetric nitro-group stretching and bending modes, are involved. This indicates that the $\text{Pt}^{\text{II}} \rightarrow \text{Pt}^{\text{IV}}$ intervalence transition, by altering the effective positive charge on each metal atom, affects the extent of $\text{Pt}(d_{xy}) \rightarrow \text{NO}_2(\pi^*)$ back bonding and thus the equilibrium geometry of the co-ordinated NO_2 group in the intervalence state. The unusually large involvement of modes of the equatorial ligands in this case is partly due to the π -acceptor nature of the nitro-group and partly to the anion-chain (rather than cation-chain) nature of the complex.

The relationship between structure and property for linear-chain halogen-bridged complexes has recently been explored by studying the one-electron band structures determined from the tight-binding scheme based on the extended Hückel method.³⁸ The treatment recognizes that, owing to the chain nature of the complexes, their band electronic structures must be taken into account. Consideration has been given to the way in which electrical properties depend on geometric distortion of the repeat unit. The intervalence transition energy is found experimentally to depend slightly on chain length, long crystals (and therefore long chains) having lower transition energies than short chains.^{23–25} This result can also be reproduced by extended Hückel-type calculations,³⁹ but only where the chain is terminated by platinum(IV) rather than by platinum(II). Since the platinum(II)-bridge bonds are the weakest in the chain, preferential cleavage at this position is to be expected, leading to just the same conclusion as to the nature of the chain terminating group.

Many other aspects of the vibrational spectra of these chain complexes have been studied recently in considerable detail. These include^{40–43} (a) force constant analysis, (Table 5), based upon the assumption that the normal modes of such complexes may be divided into chain (localized M^{IV}) modes and equatorial modes, which are almost independent local modes (note that the progression-

³⁷ R. J. H. Clark and M. Kurmoo, *J. Chem. Soc., Chem. Commun.*, 1980, 1258; R. J. H. Clark, M. Kurmoo, A. M. R. Galas, and M. B. Hursthouse, *Inorg. Chem.*, 1981, **20**, 4206.

³⁸ M.-H. Whangbo and M. J. Foshee, *Inorg. Chem.*, 1981, **20**, 113.

³⁹ C. G. Barraclough, unpublished results.

⁴⁰ C. E. Paraskevaidis and C. Papatrionfillou, *Chem. Phys. Lett.*, 1978, **58**, 301.

⁴¹ C. E. Paraskevaidis, C. Papatrionfillou, and G. C. Papavassiliou, *Chem. Phys.*, 1979, **37**, 389.

⁴² C. G. Barraclough, R. J. H. Clark, and M. Kurmoo, *J. Struct. Chem.*, 1982, **79**, 239.

⁴³ S. D. Allen, R. J. H. Clark, V. B. Croud, and M. Kurmoo, *Philos. Trans. R.Soc. London*, in press.

forming mode, ν_1 , is strictly an even parity longitudinal optical mode of $k = 0$ of the chain), (b) f.t.i.r. studies⁴³ to 20 cm^{-1} (c) studies of the dependence of ν_1 on the wavenumber of the exciting line, a phenomenon which is undoubtedly connected with the degree of electron delocalization in the chain direction,⁴⁴ cf. the behaviour of certain modes of the semiconductors Cu_2O , CdS , and CdSe .⁴⁵ E.s.r. measurements, moreover, have demonstrated that only about one platinum atom in 10^4 in these complexes has an unpaired electron (and in a d_{z^2} orbital), which suggests that this centre may be located at structure dislocations or at thermal defects in the chain.³¹ The activation energy to create the Pt^{III} sites is related to the energy required to displace the bridging halide at the defect site.

Table 5 Pt-Cl Force constants for complexes containing the $\text{trans-}[\text{Pt}^{\text{IV}}(\text{en})_2\text{Cl}_2]^{2+}$ group^a

Complex	$f_r/10^2 \text{ N m}^{-1}$	$f_{rr}/10^2 \text{ N m}^{-1}$
$[\text{Pt}(\text{en})_2\text{Cl}_2]\text{Cl}_2$	2.278	0.228
$[\text{Ni}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2][\text{ClO}_4]_4$	2.062	0.135
$[\text{Pd}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2][\text{ClO}_4]_4$	2.105	0.121
$[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2][\text{ClO}_4]_4$	1.991	0.027

^a f_r = Pt-Cl stretching force constant, f_{rr} = stretch-stretch interaction constant (Ref. 43).

Many fewer mixed-valence halogen-bridged complexes of palladium than of platinum have yet been synthesized, but those that have display broadly similar physical properties to those discussed above.⁴⁶ The ν_1 band wavenumber of the isolated $[\text{M}^{\text{IV}}(\text{LL})_2\text{X}_2]^{2+}$ entity is lowered more for palladium than for platinum on chain formation. Moreover, the intervalence band maxima, excitation profile maxima, and ν_1 values for the palladium complexes are all of lower wavenumber than those for analogous platinum complexes, even in those cases, e.g. $[\text{M}(\text{en})_2][\text{M}(\text{en})_2\text{Cl}_2][\text{ClO}_4]_4$, for which the $r(\text{M}^{\text{IV}}-\text{Cl})/r(\text{M}^{\text{II}}-\text{Cl})$ values are identical. Since the electrical conductance of these materials is believed to be phonon assisted,³⁰ low ν_1 values and low intervalence transition energies would point to higher conductance for mixed-valence palladium than platinum complexes, a conclusion in complete agreement with experiment.³¹ Such palladium complexes therefore have less localized valences than have the analogous platinum complexes. The reverse is true for mixed-metal mixed-valence chain complexes, some of which have recently been synthesized, viz. $[\text{M}^{\text{II}}(\text{en})_2][\text{Pt}^{\text{IV}}(\text{en})_2\text{Cl}_2][\text{ClO}_4]_4$, $\text{M} = \text{Ni}, \text{Pd}, \text{or Pt}$; $\text{en} = 1,2\text{-diaminoethane}$. The intervalence transitions of the mixed-metal complexes occur at higher energies than for analogous $\text{Pd}^{\text{II}}/\text{Pd}^{\text{IV}}$ or $\text{Pt}^{\text{II}}/\text{Pt}^{\text{IV}}$ complexes, implying a greater degree of valence-electron localization and lower chain-conductance for the mixed-metal derivatives. The status of possible linear-chain nickel(II)/nickel(IV) complexes seems uncertain at this stage.

A further intriguing feature of this sort of localized-valence complex is the

⁴⁴ R. J. H. Clark and M. Kurmoo, *J. Chem. Soc., Faraday Trans. 2*, 1983, **79**, 519.

⁴⁵ P. Y. Yu, in 'Topics in Current Physics', ed. K. Cho, Springer-Verlag, Berlin, Vol. 14, 1979, p. 211.

⁴⁶ R. J. H. Clark, V. B. Croud, and M. Kurmoo, *Inorg. Chem.*, in press.

prediction⁴⁷ that, on excitation within the contour of the intervalence band, each should display electronic Raman scattering of intensity comparable to, or possibly even up to 10^3 -times more intense than that of the vibrational Raman scattering already discussed. The electronic Raman scattering corresponds to transitions between the two weakly coupled potential surfaces (Figure 7). Although the analysis fails to take account of the fact that the lowest intervalence transition is from the (II,IV) to the (III,III) rather than the (IV,II) state, the broad features of the prediction appear to be correct, since an intense band akin to fluorescence has been observed at large ($\sim 13\,000\text{ cm}^{-1}$) Stokes Raman shifts from the exciting line for complexes such as $[\text{Pd}(\text{en})_2][\text{Pt}(\text{en})_2\text{Br}_2][\text{ClO}_4]_4$.⁴⁸ Both a continuous, z-polarized emission underneath the Raman bands, as well as the emission described above, have alternatively been regarded as photo-luminescence arising from the recombination of electron and hole during and after relaxation of the charge-transfer excited state into the self-trapped ($-\text{Pt}^{3+} \text{ --- Cl}^- \text{ --- Pt}^{3+} \text{ ---}$) excited state.⁴⁹ These phenomena are still under investigation.

A final point should be made regarding the difficulty in solving the X-ray crystal structures of this type of chain complex. It appears that, although any individual chain is ordered in terms of being alternately platinum(IV) and platinum(II), adjacent chains may be arbitrarily slipped by $c/2$; this leads to disorder in the directions perpendicular to the chain (c) axis and to diffuse features in the X-ray pattern. A further difficulty is caused by the fact that many such mixed-valence complexes can be formed as mixtures of conformational isomers unless the resolved diamine is used in their preparation.⁵⁰

3 Class II Three-dimensional Complexes

The structural changes on excitation to the intervalence state of those class II mixed-valence complexes which involve essentially three-dimensional lattices are much smaller than those for linear-chain (essentially one-dimensional) species, and in consequence the degree of resonance enhancement of the appropriate bands is much smaller. Thus, although complexes such as $\text{Cs}_4[\text{Sb}^{\text{III}}\text{Cl}_6][\text{Sb}^{\text{V}}\text{Cl}_6]$, $[\text{Co}(\text{NH}_3)_6]_2[\text{Pb}^{\text{II}}\text{Cl}_6][\text{Pb}^{\text{IV}}\text{Cl}_6]$, and Prussian Blue display Raman bands which are considerably enhanced at resonance with the $\text{Sb}^{\text{III}} \rightarrow \text{Sb}^{\text{V}}$ ($\nu_{\text{max.}} = 17\,900\text{ cm}^{-1}$, $\epsilon_{\text{max.}} = 110\text{ M}^{-1}\text{ cm}^{-1}$), $\text{Pb}^{\text{II}} \rightarrow \text{Pb}^{\text{IV}}$, and $\text{Fe}^{\text{II}} \rightarrow \text{Fe}^{\text{III}}$ intervalence bands respectively, the overtone and combination band progressions are short.⁵¹ Clearly, since the structural changes following the electronic transition to the intervalence state are distributed over far more bonds in three-dimensional than in one-dimensional species, each individual change is much smaller in the former case. For $\text{Cs}_4[\text{Sb}^{\text{III}}\text{Cl}_6][\text{Sb}^{\text{V}}\text{Cl}_6]$, the main progression-forming mode is ν_1 (a_{1g}) of the $[\text{SbCl}_6]^-$ ion, the subsidiary progressions being $\nu_1\nu_1 + \nu_1'$ (where ν_1' is the ν_1 (a_{1g}))

⁴⁷ K. Y. Wong and P. N. Schatz, *Chem. Phys. Lett.*, 1981, **80**, 172; K. Y. Wong, *ibid.*, 1984, **108**, 484.

⁴⁸ R. J. H. Clark and M. Kurmoo, unpublished results, 1981.

⁴⁹ H. Tanino and K. Kobayashi, *J. Phys. Soc. Jpn.*, 1983, **52**, 1446.

⁵⁰ R. J. H. Clark, M. Kurmoo, D. N. Mountney, and H. Toftlund, *J. Chem. Soc., Dalton Trans.*, 1982, 1851.

⁵¹ R. J. H. Clark and W. R. Trumble, *J. Chem. Soc., Chem. Commun.*, 1975, 318; R. J. H. Clark and W. R. Trumble, *J. Chem. Soc., Dalton Trans.*, 1976, 1145.

mode of the $[\text{SbCl}_6]^{3-}$ ion), $v_1v_1 + v_5$ (where v_5 is the t_{2g} mode of the $[\text{SbCl}_6]$ ion) and $v_1v_1 + v_L$ (where v_L is a lattice mode at 60 cm^{-1}).

The resonance Raman spectrum of the system $\text{Cs}_2[\text{Sb}^{\text{III}}_x\text{Sb}^{\text{V}}_x\text{Sn}_{1-2x}\text{Cl}_6]$, $x = 0.18$, shows host $[\text{SnCl}_6]^{2-}$ modes as well as those of the $[\text{SbCl}_6]^{3-}/[\text{SbCl}_6]$ chromophore.⁵² Since the exciting lines used had much lower wavenumbers than that of the first charge-transfer band of the $[\text{SnCl}_6]^{2-}$ ion, this result indicates the strong dynamic involvement of the host lattice during the $\text{Sb}^{\text{III}} \rightarrow \text{Sb}^{\text{V}}$ dopant electron-transfer process. Moreover, it is regarded as providing the first direct experimental observation of the dynamics associated with outer-sphere chemical activation for electron-transfer processes.

The shape of the intervalence band of a single crystal of $[\text{CH}_3\text{NH}_3]_2[\text{Sb}^{\text{III}}_x\text{Sb}^{\text{V}}_x\text{Sn}_{1-2x}\text{Cl}_6]$ between 300 and 4 K is Gaussian.⁵³ From the temperature dependence of the second moment of the band, the electron-phonon coupling constant and hence the displacement in the vibrational co-ordinate from the ground to the intervalence state can be deduced, along with the effective phonon wavenumber coupled to the transition. The latter (290 cm^{-1}) is close to the mean wavenumber of the ground state totally symmetric fundamentals of $[\text{SbCl}_6]^{3-}$ (267 cm^{-1}) and $[\text{SbCl}_6]^-$ (327 cm^{-1}). Moreover, the displacement in the vibrational co-ordinate is calculated to be *ca.* 0.19 \AA , which approaches half the difference between the Sb-Cl bond lengths ($0.262/2 = 0.131 \text{ \AA}$). It is concluded that the electron transfer in this salt is coupled to the antisymmetric combination of the two totally symmetric fundamentals mentioned above, and that the Franck-Condon factors associated with this mode are largely responsible for the breadth of the intervalence band.

It is also interesting that the mixed-valence salt $\text{Rb}_{2.67}\text{SbCl}_6$, which must involve a $[\text{SbCl}_6]^- : [\text{SbCl}_6]^{3-}$ ratio of 1:5, displays a resonance Raman spectrum closely similar to that of Cs_2SbCl_6 . Detailed studies of such salts are still in progress.

4 Complexes on the Class II/III Borderline

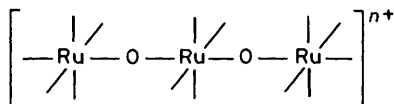
For a polyatomic molecule in which there are several totally symmetric normal modes, each will involve the motion of a large number of atoms. If the valence electrons are delocalized in the ground or excited states or in both, and the extent of delocalization is changed on electronic excitation, then many atoms need to undergo small displacements in order that the molecule may reach its new equilibrium geometry *i.e.* there must be a displacement, albeit small, of the excited-state potential minimum along several totally symmetric normal co-ordinates. This situation gives rise to the so-called 'small displacement approximation' in resonance Raman theory, and has the consequence that the Franck-Condon factors are significant for all the totally symmetric fundamentals but not for any overtones.

Mixed-valence complexes which lie near to the class II/III borderline have been shown to behave in the manner described above; thus their resonance Raman spectra are very different from those displayed by class II linear-chain complexes

⁵² H. W. Clark and B. I. Swanson, *J. Am. Chem. Soc.*, 1979, **101**, 1604.

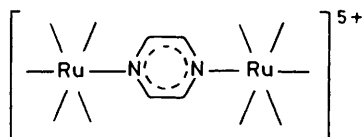
⁵³ K. Prassides and P. Day, *J. Chem. Soc., Faraday Trans. 2*, 1984, **80**, 85; see also P. Day, *Inorg. Chem.*, 1963, **2**, 452 and L. Atkinson and P. Day, *J. Chem. Soc. (A)*, 1969, 2423, 2432.

for which any structural change on excitation is confined to being along a single coordinate. Good examples of borderline complexes are provided by the cytological dyes Ruthenium Red $[\text{Ru}_3\text{O}_2(\text{NH}_3)_{14}]^{6+}$ and Ruthenium Brown $[\text{Ru}_3\text{O}_2(\text{NH}_3)_{14}]^{7+}$ and by related 1,2-diaminoethane-substituted species.^{53,54} These ions are linear, and probably have the eclipsed configuration in solution, *viz.*



All the totally symmetric skeletal modes of these complexes are enhanced at resonance with the lowest $e_u^* \rightarrow e_g^*$, π -type transition ($\tilde{\nu}_{\text{max.}} = 18\,700\text{ cm}^{-1}$, $\epsilon_{\text{max.}} = 7 \times 10^4\text{ M}^{-1}\text{ cm}^{-1}$);⁵⁵ moreover, no overtones of significant intensity are detected. Thus although Ruthenium Red formally involves $\text{Ru}^{\text{III}}\text{Ru}^{\text{IV}}\text{Ru}^{\text{III}}$, it behaves virtually as though it were a delocalized-valence complex with equivalent (and therefore non-integral) metal-ion valences of approximately 3.33. Ruthenium Brown, for which the analogous transition lies at $21\,800\text{ cm}^{-1}$ ($\epsilon_{\text{max.}} = 8 \times 10^4\text{ M}^{-1}\text{ cm}^{-1}$), formally involves $\text{Ru}^{\text{III}}\text{Ru}^{\text{IV}}\text{Ru}^{\text{IV}}$ but behaves likewise as a delocalized-valence complex with nearly equivalent metal-ion valences of approximately 3.67.

Another complex about which there has been considerable controversy regarding its classification, virtually since its discovery in 1969, is the Creutz-Taube ion,¹⁵ whose structure (as well as those of its 4+ and 6+ analogues)⁵⁶ is illustrated below:



Note that the plane of the bridging pyrazine ligand bisects the angle between the equatorially co-ordinated $\text{NH}_3\text{---Ru---NH}_3$ groups. The controversy relates to whether the complex should be regarded as class II, trapped valence ($\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$) or as class III, delocalized valence, possible delocalization of the odd d_π electron being effected *via* the pyrazine π^* orbitals. Many studies of different salts of this ion, involving electronic, photoelectron, infrared, Raman, resonance Raman, Mössbauer, and electron spin resonance spectroscopy and magnetic measurements, although favouring the delocalized picture, have not provided a definitive answer to this question.¹¹ Part of the problem relates to the sensitivity of the ion to photodegradation, an effect which seriously compromised many of the early measurements. Moreover, even the most recent study, an extensive collaborative

⁵⁴ J. R. Campbell, R. J. H. Clark, W. P. Griffith, and J. Hall, *J. Chem. Soc., Dalton Trans.*, 1980, 2228.
R. J. H. Clark and T. J. Dines, *Mol. Phys.*, 1981, **42**, 193.

⁵⁵ R. J. H. Clark and M. Kurmoo, unpublished work.

⁵⁶ U. Fürholz, A. Ludi, H.-B. Burgi, F. E. Wagner, A. Stebler, J. H. Ammeter, E. Krausz, R. J. H. Clark, and M. J. Stead, *J. Am. Chem. Soc.*, 1984, **106**, 121.

one involving many techniques, was not wholly conclusive on this matter, although the weight of evidence remains in favour of the delocalized-valence description. It is possible that the Creutz-Taube ion is class IIIA on a long time scale (*e.g.* crystallographic or nuclear magnetic resonance) but class II on a short time-scale (*e.g.* photoelectron). What is certain, however, in view of the conflicting results on this matter, is that the complex must be close to the class II/III borderline. It is also worth noting that there are only slight ($\approx 0.1 \text{ \AA}$) changes to any of the Ru-N bond lengths on one-electron oxidation or reduction of the Creutz-Taube ion.⁵⁶

Resonance Raman studies of the Creutz-Taube ion have so far been restricted to the use of exciting lines with wavenumbers falling within the contour of the $\text{Ru}(d_{\pi}) \rightarrow \text{pyrazine}(\pi^*)$ charge-transfer transition, which reaches a maximum at *ca.* 20 000 cm^{-1} .⁵⁷ This leads to resonance enhancement of many skeletal modes of the complex, in a manner similar to that observed for the mononuclear complexes⁵⁸ $[\text{Ru}^{\text{II}}(\text{NH}_3)_5\text{L}][\text{PF}_6]_2$ (L = 4-cyano-1-methylpyridinium or 1-methyl-4,4'-bipyridinium) and $[\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{L}]\text{Cl}_3$ (L = 4-dimethylaminopyridine) at resonance with the analogous $\text{Ru}(d_{\pi}) \rightarrow \text{pyrazine}(\pi^*)$ transition.

It has not yet proved possible to irradiate within the contour of the intervalence band of the Creutz-Taube ion ($\tilde{\nu}_{\text{max.}} = 6\,370 \text{ cm}^{-1}$, $\epsilon_{\text{max.}} = 5\,000 \text{ M}^{-1} \text{ cm}^{-1}$) owing to the lack of exciting lines in, and detectors for, this low-wavenumber region. This is unfortunate, since intriguing predictions as to the nature of the Raman spectrum of this ion at resonance with the intervalence transition have been made⁵⁹ and cannot at this stage be tested. One possibility for a suitable exciting line is the second Stokes hydrogen-shifted emission (*ca.* $-8\,000 \text{ cm}^{-1}$ shifted) from Rhodamine 640 (with or without Oxazine 720), the pump line being provided by a frequency doubled Nd:YAG laser (532 nm). This would provide radiation in the $6\,000 \text{ cm}^{-1}$ region; however, the technical problems associated with this experiment have not yet been fully overcome.

5 Class III A

Simple Radical Species.—The most obvious species which could be regarded as class IIIA, delocalized valence, in type are simple radical cations or anions. It is, of course, a matter of taste as to whether or not such species should be so regarded, but they clearly are limiting versions of this type. Some such species have been first characterized by electronic and resonance Raman spectroscopy, others have had various features of their structures and bonding clarified by such studies.

The Xe_2^+ ion is an example of an ion first characterized in a condensed phase by the techniques mentioned above (and others). The ion is prepared by passing xenon gas through the orange solution of $\text{O}_2^+[\text{SbF}_6]^-$ in SbF_5 , whereupon the colour changes to green ($\lambda_{\text{max.}} = 710 \text{ nm}$, $\epsilon_{\text{max.}} = 6\,000 \text{ M}^{-1} \text{ cm}^{-1}$). Use of 530.8 nm excitation, which corresponds to an absorption minimum for the ion, yields an unspectacular Raman spectrum dominated by bands attributed to the SbF stretching modes of the solvent (Figure 9). However, by changing to 676.4 nm

⁵⁷ M. J. Stead, Ph.D. thesis, University of London, 1983; R. J. H. Clark and M. J. Stead, to be published.

⁵⁸ R. J. H. Clark and M. J. Stead, *J. Chem. Soc., Dalton Trans.*, 1981, 1760.

⁵⁹ K. Y. Wong and P. N. Schatz, *Chem. Phys. Lett.*, 1980, 73, 456.

excitation, which falls within the contour of the 710 nm band of the chromophore, a much more intense Raman spectrum is obtained, dominated by a progression of four members (all polarized) in a mode of wavenumber 123 cm^{-1} . The latter is insensitive to ^{18}O substitution, but is lowered by 2.4 cm^{-1} on substituting natural abundance xenon (RAM = 131.3) by ^{136}Xe .⁶⁰ These features allow the chromophore to be identified as Xe_2^+ , the first noble gas cation to be characterized in a condensed phase (as $\text{Xe}_2^+[\text{Sb}_2\text{F}_{11}]^-$). The transition with which the 676.4 nm line is in resonance is considered to be ${}^2\Sigma_{\frac{1}{2}u}^+ \rightarrow {}^2\Pi_{\frac{1}{2}g}$, by analogy with the situation for the isoelectronic ion I_2^- , for which very similar electronic and resonance Raman spectra have been obtained (Table 6). Both Xe_2^+ and I_2^- have much lower vibrational frequencies than has I_2 , consistent with the molecular orbital picture of the two ions as being held together by a bond of order one half, whereas I_2 itself is single bonded. These ions can be regarded as examples of $\text{Xe}^{+0.5}$ and $\text{I}^{-0.5}$, respectively. Obviously many polyiodides and other related species are of a similar type.

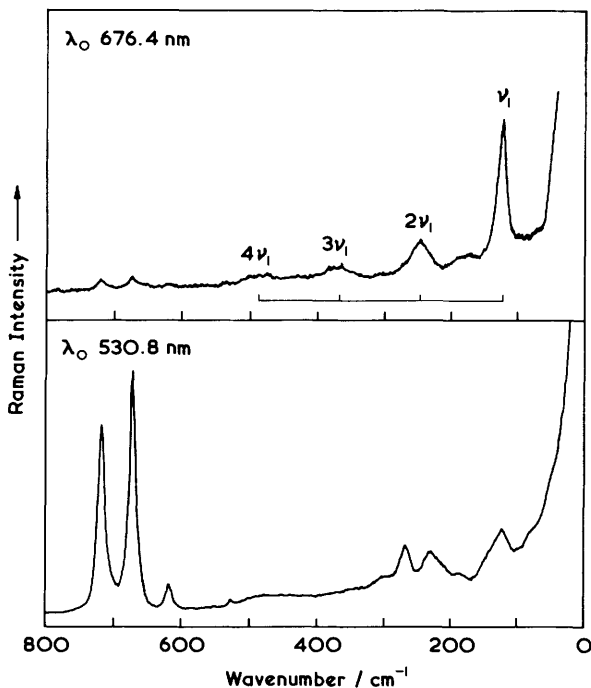


Figure 9 Raman spectrum of $[\text{Xe}_2^+][\text{Sb}_2\text{F}_{11}]^-$ in SbF_5 solution both on ($\lambda_0 = 676.4\text{ nm}$ excitation) and off ($\lambda_0 = 530.8\text{ nm}$ excitation) resonance with the $\pi \rightarrow \pi^*$ transition of lowest energy of the cation

⁶⁰ L. Stein, J. R. Norris, A. J. Downs, and A. R. Minihan, *J. Chem. Soc., Chem. Commun.*, 1978, 502; R. J. H. Clark and D. G. Cobbold, unpublished work, 1978.

Table 6 Spectroscopic data on related diatomic species

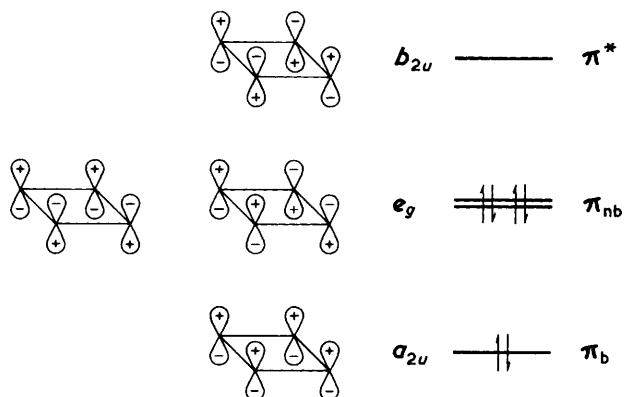
Species	Colour	Ground State	$\lambda_{\text{max.}}/\text{nm}$	Overtone	ω_e/cm^{-1}	$\omega_e x_e/\text{cm}^{-1}$	State
Xe_2^+	green	$^2\Sigma_{\frac{1}{2}u}^+$	710 ^a	4	123	0 ± 1	<i>b</i>
I_2^-	green	$^2\Sigma_{\frac{1}{2}u}^+$	800	6	114.2	0.50	<i>c</i>
I_2	red-violet	$^1\Sigma_{0g}^+$	505	20	214.5	0.61	<i>d</i>

^a $\epsilon_{\text{max}} \sim 6000 \text{ M}^{-1} \text{ cm}^{-1}$. ^b $[\text{Sb}_2\text{F}_{11}]^-$ salt, in SbF_5 solution. ^c K^+ salt, the resonance Raman spectrum being measured on an argon matrix of the salt at ca. 12 K. W. F. Howard and L. Andrews, *J. Am. Chem. Soc.*, 1975, **97**, 2956; L. Andrews, *J. Am. Chem. Soc.*, 1976, **98**, 2152. ^d Gas phase data: R. F. Barrow and K. K. Yee, *J. Chem. Soc., Faraday Trans. 2*, 1973, **69**, 684.

Several other simple ions provide examples of elements in the +0.5 oxidation state. Thus the cations S_4^{2+} , Se_4^{2+} , and Te_4^{2+} involve the square planar $\text{M}-\text{M}^{2+}$

6π -electron system $|\ 6\pi \ |$, which has D_{4h} symmetry. They have all recently been $\text{M}-\text{M}$

characterized in sulphuric acid or oleum media by resonance Raman techniques (which are remarkably adept at probing the nature of chromophores in hostile environments). All exhibit progressions in the $\nu_1 (a_{1g})$ stretching mode at resonance with the $^1A_{1g} \rightarrow ^1E_u[\pi(e_g) \rightarrow \pi^*(b_{2u})]$ transition, the electric-dipole allowed one of lowest wavenumber, which maximizes at 330 nm for S_4^{2+} , 410 nm for Se_4^{2+} , and 510 nm for Te_4^{2+} (Figure 10).^{61,62} Since in these cases there is only a single co-ordinate, Q_1 , along which any substantial structural change could be effected on excitation, this type of species yields resonance Raman spectra similar to those of linear-chain, class II species for which likewise only a single co-ordinate is affected by electronic excitation. Some spectroscopic data on these intriguing ions are given in Table 7.

**Figure 10** π -Molecular orbital scheme for the 6π -electron species M_4^{2+}

⁶¹ R. J. H. Clark, T. J. Dines, and L. T. H. Ferris, *J. Chem. Soc., Dalton Trans.*, 1982, 2237.

⁶² R. C. Burns and R. J. Gillespie, *Inorg. Chem.*, 1982, **21**, 3877.

Table 7 Spectroscopic data on S_4^{2+} , Se_4^{2+} , and Te_4^{2+} ^a

Physical quantity	Form	S_4^{2+} (65% oleum)	Se_4^{2+} (25% oleum)	Te_4^{2+} (H_2SO_4)
$\nu_1(a_{1g})/cm^{-1}$		583.6	321.3	219
$\nu_2(b_{1g})/cm^{-1}$		371.2	182.3	109
$\nu_3(b_{2g})/cm^{-1}$		598.1	321.3	219
$\nu_5(e_u)/cm^{-1}$		542	302	187
$\lambda_{max.}(\pi \rightarrow \pi^*)/nm$		330	410	510
$\epsilon_{max.}/M^{-1} cm^{-1}$		475	5 900	5 000
Progression length ^b		$6\nu_1$	$5\nu_1$	$6\nu_1$
ω_1/cm^{-1}		584.7	321.8	219.5
x_{11}/cm^{-1}		-0.35	-0.55	-0.30
$f/10^2 N m^{-1}$ ^c		2.78	2.10	1.45

^a Ref. 70. ^b At resonance with the $\pi \rightarrow \pi^*$ transition indicated; these are analogous transitions since the m.c.d. spectra of the ions in this region are identical to each other in form, magnitude, and sign. P. J. Stephens, *Chem. Comm.*, 1969, 1496. ^c f = stretching force constant.

Other simple sulphur ions, but anions in this case, have been shown by electron spin resonance, electronic and resonance Raman techniques to be responsible for the intense colours generated in many sulphur-containing media. The blue colour formed when alkali-metal polysulphides are dissolved in highly polar solvents such as dimethylformamide or hexa-methylphosphoramide is now known to be due to the S_3^- ion, a radical anion with an SSS angle of 105° and $\lambda_{max.} = 600$ nm, $\epsilon_{max.} = 10^4 M^{-1} cm^{-1}$. The same species is responsible for the blue colour formed by sulphur in a LiCl-KCl eutectic, in CsCl-AlCl₃ or KNCS melts, in the aluminosilicate mineral *lapis lazuli*, and in its synthetic equivalent Ultramarine Blue.⁶³⁻⁷⁰ For over 5 000 years *lapis lazuli* has been prized as a semi-precious gemstone and as a rich blue pigment for oil-paintings. Ultramarine Blue, which has been manufactured since 1828 for its pigmentary properties, contains the S_3^- ion trapped at up to 50% occupancy at the cubic sites in the aluminosilicate framework. The radical nature of the chromophore is apparent from the e.s.r. spectrum of Ultramarine Blue, and the chromophore itself can be identified from the Raman band progression (fundamental = $550 cm^{-1}$) observed at resonance with the 600 nm electronic band.

⁶³ W. Holzer, W. F. Murphy, and H. J. Bernstein, *J. Mol. Spectrosc.*, 1969, **32**, 13.

⁶⁴ F. Seel and H. J. Güttler, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 420.

⁶⁵ R. J. H. Clark and M. L. Franks, *Chem. Phys. Lett.*, 1975, **34**, 69.

⁶⁶ T. Chivers in 'New Uses of Sulphur', ed. J. R. West, American Chemical Society, Washington D.C., *Adv. Chem. Ser.* No. 140, p. 499.

⁶⁷ R. J. H. Clark and D. G. Cobbold, *Inorg. Chem.*, 1978, **17**, 3169.

⁶⁸ R. W. Berg, N. J. Bjerrum, G. N. Papatheodorou, and S. von Winbush, *Inorg. Nucl. Chem. Lett.*, 1980, **16**, 201.

⁶⁹ R. J. H. Clark, D. P. Fairclough, and M. Kurmoo, in 'Time-Resolved Vibrational Spectroscopy', ed. G. H. Atkinson, Academic Press, 1983, p. 213.

⁷⁰ R. J. H. Clark, T. J. Dines, and M. Kurmoo, *Inorg. Chem.*, 1983, **22**, 2766.

By various modifications to the preparative procedures it is possible to synthesize other pigmentary materials, known as Ultramarine Green, many different shades of Ultramarine Violet, and Ultramarine Pink. These clearly contain additional chromophores. One of these, with its lowest allowed electronic transition at 380—400 nm, has been identified as the S_2^- ion; this species is present in small amounts in Ultramarine Blue, Violet, and Pink, but in much larger amounts in Ultramarine Green. The third species, principally responsible for the colour of Ultramarine Pink ($\lambda_{\max.} = 520$ nm) has not yet been certainly identified,

Table 8 Spectroscopic properties of diatomic sulphur and selenium species

Species	Electronic state	ω_e/cm^{-1}	$\omega_e x_e/\text{cm}^{-1}$	$\delta/\text{\AA}^a$
3S_2	${}^3\Sigma_g^-$	725.68	2.852	0.291
	${}^3\Sigma_u^-$	434.0	2.75	
S_2^-	${}^2\Pi_{3g}$	597.0	2.50	0.30
	${}^2\Pi_u$	360	—	
${}^{80}Se_2$	${}^1\Sigma_g^+$	391.77	1.06	0.293
	${}^1\Sigma_u^+$	281.11	2.65	
Se_2^-	${}^2\Pi_{3g}$	329.6	0.70	0.32
	${}^2\Pi_u$	216	—	

^a δ = bond length change on excitation, as deduced for neutral species by gas phase electronic spectroscopy, and for ions from Raman band excitation profiles obtained with exciting lines near resonance with the specified excited state (Ref. 70).

though it may be S_4^- . The Se_2^- ion has likewise been identified as the chromophore present in Selenium Ultramarine ($\lambda_{\max.} = 490$ nm). Various spectroscopic properties of these diatomic ions are compared with those of the analogous neutral molecules in Table 8. The additional electron in the case of the radicals clearly enters an antibonding orbital, in view of the large drop in vibrational frequency on passing from the neutral species to the anion, but the bond length elongation on excitation to the lowest excited state is in all cases very similar. Thus the key chromophores in all the ultramarines are simple class IIIA radical anions. What feature of the Ultramarine lattice is responsible for its ability to trap and stabilize these normally unstable radicals is not known. Yet the fact that it does is entirely responsible for our interest in these materials as pigments for paints, plastics, rubbers, talcum powders, and eye shadows!

Cluster Species.—Of the many different sorts of cluster species known, it is arguable that the most important are the cubane-type FeS clusters of the sort $[Fe_4S_4(SR)_4]^{2-}$, R = alkyl or aryl, since these have been shown to be close representations, or synthetic analogues, of the redox centres present in a variety of different iron-sulphur proteins. Such complexes act as structural models and indicators of the oxidation levels of the protein active-sites.^{71,72} In particular, these prototypes possess a common oxidation level with oxidized ferredoxin (Fd_{ox}) and

⁷¹ R. H. Holm, *Endeavour*, 1975, 38.

⁷² R. H. Holm, *Chem. Soc. Rev.*, 1981, 10, 455.

chromatium (HP_{red}) in that all contain 2Fe^{II} and 2Fe^{III}. The key question, in the context of the present review, is whether the valence electrons are localized or delocalized. In fact, a variety of physical techniques, in particular Mössbauer, electron spin resonance and nuclear magnetic resonance spectroscopy but more recently resonance Raman spectroscopy, have demonstrated that all the metal atom sites are equivalent and thus that such clusters are electronically fully delocalized rather than trapped-valence species.^{73,74} This result ties in well with the most important biophysical property of iron-sulphur proteins, which is that of electron transfer; rapid electron transfer is aided if the geometrical rearrangements around the metal-ion site are small, as implied by the resonance Raman results. The complex in question thus involves Fe^{+2.5}, and it can be one-electron oxidized or reduced to a species involving Fe^{2.75} or Fe^{2.25}, respectively.

The [MS₄]²⁻ ions, M = Mo or W, which are known to display long progressions in the $\nu_1(a_1)$ mode at resonance with the S(p_π) → M(d_π) charge-transfer band,^{34,35,75} do not behave likewise when they are incorporated in dinuclear species such as [(PhS)₂FeS₂MS₂]²⁻.⁷⁶ At resonance with the corresponding electronic band of such species, all the skeletal fundamentals (and not the overtones) are enhanced, suggesting that the valence electrons are, in this case, largely delocalized over the whole complex ion, a conclusion also suggested by Mössbauer results. The intriguing question as to the degree of delocalization of the valence electrons in cluster species involving a hetero atom, e.g. Fe₃Mo, Fe₃W, Cu₃Mo, etc.,^{77,78} remains to be investigated.

OTTLE (optically transparent thin layer electrochemical) cells may permit the *in situ* spectroscopic study of electrochemically generated species, a technique of immense but as yet largely unexplored promise. One application already investigated has been to the study of the electronic spectrum of incompletely reduced ruthenium bipyridyl and related species. The new absorption band generated on reduction at ca. 4 000 cm⁻¹ ($\epsilon = 100\text{--}345 \text{ M}^{-1} \text{ cm}^{-1}$) has been interpreted as arising from the ligand-based intervalence charge-transfer transition, bipy⁻ → bipy.⁷⁹

There are also series of mixed-valence ruthenium complexes, the class of which depends on the closeness of matching of the ligands attached to each metal atom. Thus extensive electrochemical studies have established the existence of several confacial bioctahedral complexes of the sorts [L₃RuCl₃RuL₃]²⁺ and [L_{3-x}Cl_xRuCl₃RuCl_{3-y}L_{3-y}]ⁿ⁺, where L = PEt₂Ph, As(tol)₃, or PPh₃, which display at least one, and generally two, stepwise reversible one-electron transfer reactions without there being any change in gross molecular structure.⁸⁰ One

⁷³ D. W. Stephan, G. C. Papaefthymion, R. B. Frankel, and R. H. Holm, *Inorg. Chem.*, 1983, **22**, 1550.

⁷⁴ G. D. Friesen, J. W. McDonald, W. E. Newton, W. B. Euler, and B. M. Hoffman, *Inorg. Chem.*, 1983, **22**, 2202.

⁷⁵ R. J. H. Clark, ACS Symposium Series, No. 211. 'Inorganic Chemistry: Toward the 21st Century', ed. M. H. Chisholm, 1983, p. 509.

⁷⁶ R. J. H. Clark, T. J. Dines, and G. P. Proud, *J. Chem. Soc., Dalton Trans.*, 1983, 2299.

⁷⁷ C. D. Garner, to be published.

⁷⁸ A. Müller, E. Diemann, R. Jostes, and H. Bögge, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 934.

⁷⁹ G. A. Heath, L. J. Yellowlees, and P. S. Bratermann, *Chem. Phys. Lett.*, 1982, **92**, 646.

⁸⁰ G. A. Heath, A. J. Lindsay, T. A. Stevenson, and D. K. Vattis, *J. Organomet. Chem.*, 1982, **233**, 353.

important parameter which helps to determine the physical properties of these complexes is the degree of asymmetry, defined to be $y - x$.

Analysis of the wavenumbers and intensities of the intervalence charge-transfer bands of the mixed-valence $\text{Ru}_2^{\text{II,III}}$, versions of this type of complex (bands which are absent from the spectra of their $\text{Ru}_2^{\text{II,II}}$ and $\text{Ru}_2^{\text{III,III}}$ congeners) indicates that the extent of valence-electron delocalization depends on the degree of asymmetry (*i.e.* on $y - x$) and on the basicity of the terminal ligands, L. Where $y - x$ is zero, as for $[(\text{PEt}_2\text{Ph})_3\text{RuCl}_3\text{Ru}(\text{PEt}_2\text{Ph})_3]^{2+}$, $[(\text{As toI}_3)_2\text{ClRuCl}_3\text{RuCl}(\text{As toI}_3)_2]$ and also for the species $[(\text{NH}_3)_3\text{RuCl}_3\text{Ru}(\text{NH}_3)_3]^{2+}$, (thought to be akin to the so-called 'Ruthenium Blue')^{81,82} the intervalence band is intense and of low wavenumber (4 350, 5 900, and 7 150 cm^{-1} , respectively). Such species are regarded as highly delocalized. However, as the degree of asymmetry is increased, *i.e.* the environments of the two metal atoms become different, the complex ions become trapped-valence systems, as judged by the much lower intensities and higher wavenumbers (*e.g.* 13 500 cm^{-1} for $[(\text{PEt}_2\text{Ph})_3\text{RuCl}_3\text{RuCl}_2(\text{PEt}_2\text{Ph})_3]$) of their intervalence bands. Extensive spectroelectrochemical studies of these and related systems are in hand.

Another type of cluster in which the question of electron delocalization in mixed-valence species is important is that of the molybdenum hetero- and isopolyanions based on the Lindqvist (Mo_6O_{19}) and Keggin ($\text{XMo}_{12}\text{O}_{40}$) structures ($\text{X} = \text{Si, Ge, P, or As}$). The reduced species, the heteropolyblues (containing Mo^{V} as well as Mo^{VI}) have been studied by both e.s.r. and electronic spectroscopy in order to assess the degree of delocalization of the additional electron. All these species appear to be valence trapped on the e.s.r. timescale at sufficiently low temperatures, even $[\text{Mo}_6\text{O}_{19}]^{3-}$ which is thus $[\text{Mo}^{\text{V}}\text{Mo}^{\text{VI}}_5\text{O}_{19}]^{3-}$ at 77 K (it exhibits a six-line hyperfine structure at this temperature).⁸³ Owing to the very short timescale of u.v.-visible spectroscopy, the mobile electron appears trapped as assessed by this technique, even at room temperature. The reference materials are $[\text{Mo}^{\text{V}}\text{W}^{\text{VI}}_5\text{O}_{19}]^{3-}$ and $\alpha\text{-}[\text{SiMo}^{\text{V}}\text{W}^{\text{VI}}_{11}\text{O}_{40}]^{5-}$, in which no homonuclear electron transfer process can take place. For some typical homonuclear systems, *e.g.* $[\text{PMo}_{12}\text{O}_{40}]^{4-}$ and $[\text{GeMo}_{12}\text{O}_{40}]^{5-}$, computer simulation of the e.s.r. spectrum over a wide temperature range has allowed the rate of thermal electron-transfer and the corresponding activation energy to be calculated. In particular, the broadening of e.s.r. spectra with increasing temperature indicates that thermal electron-delocalisation occurs when the paramagnetic Mo^{5+} ion is surrounded by Mo^{6+} ions; this is caused by electron hopping between sites. At room temperature it is not possible to detect an e.s.r.-distinguishable Mo^{V} site. Analysis of the e.s.r. spectra indicates that the valence electrons are more delocalized in the Keggin than in the Lindqvist structure, presumably due to the corner-sharing mode of junction which is specific to the former.

⁸¹ E. E. Mercer and L. W. Gray, *J. Am. Chem. Soc.*, 1972, **94**, 6426.

⁸² E. E. Mercer and P. E. Dumas, *Inorg. Chem.*, 1971, **10**, 2755.

⁸³ C. Sanchez, J. Livage, J. P. Launay, M. Fournier, and Y. Jeannin, *J. Am. Chem. Soc.*, 1982, **104**, 3194.

6 Class IIIB Species

Few Raman studies of mixed-valence complexes of this class have yet been attempted. The most interesting candidates in this context, KCP and $K_{1.75}Pt(CN)_4 \cdot 1.5H_2O$, are difficult to study owing to their metallic reflectivity and to their tendency to dehydrate on being warmed. Although their Raman spectra have been obtained, these do not show any resonance effects.⁸⁴⁻⁸⁶

Partial oxidation of Magnus Green, $[Pt(NH_3)_4][PtCl_4]$, yields a variety of products, some of which apparently involve directly metal-metal bonded species, have room temperature conductance of $\sim 10^{-2} \Omega^{-1} cm^{-1}$, and a non-integral platinum oxidation state of 2.41.⁸⁷ These materials are interesting but, as yet, poorly defined. One of the products of this oxidation is the photochromic salt $[Pt(NH_3)_4][Pt(NH_3)_4Cl_2][HSO_4]_4$, as established by resonance Raman⁸⁸ and X-ray work.^{89,90}

7 Conclusion

The very diverse features of mixed-valence chemistry will undoubtedly continue to attract the interest of synthetic chemists, whether based in University or in Industry, for many years to come.⁹¹ Certainly the search for materials with useful properties is a major challenge to chemists of all persuasions, *i.e.* not only to those seeking new materials but also to those interested in understanding the basis of, and inter-relationship between, physical properties.⁹¹ The further application of physical techniques to the study and classification of mixed-valence compounds is a matter of considerable importance to inorganic chemists, geochemists, and bioinorganic chemists alike.

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⁸⁴ E. F. Steigmeier, R. London, G. Harbeke, H. Andersset, and G. Scheiber, *Solid State Commun.*, 1975, **17**, 1447.

⁸⁵ E. F. Steigmeier, D. Baeriswyl, G. Harbeke, H. Andersset, and G. Scheiber, *Solid State Commun.*, 1976, **20**, 661.

⁸⁶ E. F. Steigmeier, D. Baeriswyl, H. Andersset, and J. M. Williams, in *Lecture Notes in Physics*, ed. S. Barisić, A. Bjeliš, J. R. Cooper, and B. Leontić, Springer, 1979, p. 229.

⁸⁷ J.-P. Catinat, T. Robert, and G. Offergeld, *J. Chem. Soc., Chem. Commun.*, 1983, 1310.

⁸⁸ R. J. H. Clark and M. Kurmoo, *J. Chem. Soc., Dalton Trans.*, 1982, 2515.

⁸⁹ R. J. H. Clark, M. Kurmoo, A. M. R. Galas, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1982, 2505.

⁹⁰ P. E. Fanwick and J. L. Huckaby, *Inorg. Chem.*, 1982, **21**, 3067.

⁹¹ P. Day, *Chem. Br.*, 1983, 306.