Mixed valence: origins and developments

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Mixed-valence compounds were recognized by chemists more than a century ago for their unusual colours and stoichiometries, but it was just 40 years ago that two seminal articles brought together the then available evidence. These articles laid the foundations for understanding the physical properties of such compounds and how the latter correlate with molecular and crystal structures. This introduction to a discussion meeting briefly surveys the history of mixed valence and sets in context contributions to the discussion describing current work in the field.

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Valence is a word that was not used much by chemists at the beginning twenty-first century, although it was once employed very widely to count the electrons forming bonds between atoms (Pauling’s now rather defunct valence bond model for example, Pauling 1960). To describe the effective number of electrons associated with a given atom when found inside a molecule or solid (in particular d-electrons in transition metal compounds), the phrase ‘oxidation state’ has largely supplanted it (Jorgensen 1969). On the other hand, it does continue in everyday use as part of the term ‘mixed valence’, although ‘mixed oxidation state’ perhaps conveys a clearer idea about what is signified, namely the situation in which the number of electrons assigned to each atom is not integral, e.g. as in Fe3O4. The word ‘mixed’ also begs a number of questions—to what extent are the oxidation states of the different atoms mixed: could they not just be integers but different from one atom to another of the same element? And if they are integral but different, can they interchange? It is significant that one of the earliest phrases attached to the phenomenon that we now call mixed valence, nearly one hundred years ago, was ‘oscillating valency’ (Hofmann & Hoeschele 1915). Finally, it is worth noting that it takes at least two atoms of the same element in one molecule or lattice before their valences (or oxidation states) can mix. Therefore, at once the world of mononuclear transition metal complexes so beloved of the protagonists of ligand field theory is left behind for the wider horizons of polynuclear complexes and aggregates.

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One contribution of 15 to a Discussion Meeting Issue ‘Mixed valency’.
Two situations, both immediately evident from the stoichiometric chemical formula derived from elemental analysis, serve to point up the existence of mixed valence in a compound. On the one hand, an empirical formula that, on the assumption the anions are closed-shell, leads to a non-integral mean cation oxidation state may do this: $\text{AFe}_2(\text{C}_2\text{O}_4)_3$ would be an example, where A is an organic cation such as $\text{[P(C}_6\text{H}_5)_4]^+$ (Mathoniere et al. 1996). On the other hand, the mean metal oxidation state may be integral but highly unusual, even implausible, for the element in question. An example would be $\text{Pd(NH}_3)_2\text{Cl}_3$ (Sainte-Claire Deville & Debray 1878), since the ‘normal’ oxidation states of Pd are $0$, $+2$ and $+4$. One of the first groups of mixed-valence compounds studied in detail (Day 1963) were of the latter type since they appeared to contain Sb in the $+4$ oxidation state when the more usual oxidation states for that element are $+3$ and $+5$. Clearly, a $1:1$ ratio of the latter would lead to the stoichiometry observed in, say, $\text{Cs}_2\text{SbCl}_6$.

Intense colour often, but by no means always, accompanies mixed valence and $\text{Cs}_2\text{SbCl}_6$ is dark blue, a highly unusual colour for a post-transition metal compound. Indeed, it was owing to their colours that mixed-valence compounds came to the note of chemists long before the paler and more subtle colours of many other transition metal compounds were remarked upon. Prussian blue, which dates from 1704, is a prime example and $\text{Cs}_2\text{SbCl}_6$ was first reported over one hundred years ago. Indeed, it was by measuring the electronic spectra of fully oxidized, fully reduced and mixed-valence states of complex ions that the latter could be identified as containing well-defined species with an intermediate electronic state. Day and colleagues (Day 1963; Culpin et al. 1965), Robin (1962) and Allen & Hush (1967) prepared a number of such systems in the solid state and showed that in every case the electronic spectrum of the mixed-valence compound was approximately a superposition of those of the fully oxidized and fully reduced species together with at least one new excitation, responsible for the characteristic mixed-valence colour. This was identified as a phonon-coupled outer- or inner-sphere metal-to-metal electronic transition and was given the name of intervalence transfer (IT) excitation (Allen & Hush 1967). In particular, the spectra of Prussian blue (Robin 1962), mixed-valence Cu(I,II) chloro-complexes (Culpin et al. 1965) and Sb(III, V) systems diluted in $\text{M}_2\text{Sn(IV)}\text{Cl}_6$ (Day 1963; Allen & Hush 1967) were unambiguously interpreted in this way. The tool for most of these early measurements was diffuse reflectance spectroscopy; however, in a polarized transmission spectrum of the Fe(II,III) mixed-valence mineral vivianite (Allen & Hush 1967) all the bands could be assigned as either IT or ligand field transitions. This was the first such study of a mineral. The spectra of a number of rock-forming minerals whose colour is often due to intervalence absorption were also obtained (Allen & Hush 1967); this was the inception of subsequent detailed electronic spectroscopy of such minerals carried out by Burns (1970).

In 1967, almost simultaneously with Allen & Hush (1967), Robin & Day (1967) published an extensive survey of mixed-valence systems encompassing the entire periodic table and proposed that the properties of such compounds could be classified according to their molecular or crystal structure. If a metal M can appear in two different oxidation states (say P and Q) and it occupies two identifiable sites in the crystal (A and B), the extent of mixing between the two Heitler–London configurations $\text{M}_A^P\text{M}_B^Q$ and $\text{M}_A^Q\text{M}_B^P$ will be reflected in how distinguishable the two sites are crystallographically. If the sites are very different the electrons...
will be completely trapped (class 1). If, on the other hand, they are completely indistinguishable, the compound is assigned to class 3, with a genuinely non-integral valence. Between these two extremes lies a range of intermediate cases (class 2) in which the environments of the sites A and B are distinguishable, but not very different. This classification was used qualitatively to unify the observed physical properties (particularly spectroscopic, electrical and magnetic) of mixed-valence solids. In the succeeding 40 years, there has been an explosion of interest in the electronic structure of mixed-valence systems, which may or may not be infinite lattice solids, and the above classification is generally broadened to describe the electronic state of any mixed-valence ion, molecule or solid in kinetic terms, class 2 systems having ground states that are localized on the vibrational time scale and class 3 delocalized on this scale.

The systems discussed theoretically by Allen & Hush (1967) belong exclusively to class 2, and thus should exhibit measurable thermal electron transfer. The molecular orbital theory of the corresponding IT optical transition which, like that of the thermal transition, can be formulated in terms of linear electron–phonon coupling, was also given by Hush (1967). According to this theory, the envelope of the intervalence electronic absorption band yields three parameters defining the dynamics of thermal transfer as well as that of the corresponding optical transfer. From the second moment of the absorption envelope (approx. the band width), the reorganization or electron–phonon coupling energy ℓ is deduced. From this and the first moment (approx. the energy of the band maximum), the overall free energy $E_o$ ('driving force') is obtained, and finally, the zeroth moment (intensity) provides an estimate of the electronic coupling $J$ between the centres. These three quantities are sufficient to predict the corresponding thermal transfer rate either for adiabatic or non-adiabatic transfers in the semi-classical (Marcus 1956) or molecular orbital (Hush 1961) formalisms. The same quantities also determine the nature and stability of the ground state. For Prussian blue, for example, the single-photon allowed intervalence process is approximately (Robin 1962)

$$[\text{Fe(III)}t_{2g}^{3}e_{g}^{2}(6A_{1g}), \text{Fe(II)}t_{2g}^{6}(1A_{1g})](6A_{1g}) + hv$$

$$\rightarrow [\text{Fe(II)}t_{2g}^{4}e_{g}^{2}(5T_{2g}), \text{Fe(III)}t_{2g}^{5}(2T_{2g})](6T_{1u}).$$

From the value of $J$ estimated from the optical spectrum, it was concluded that the electron being transferred is at least 90% located on the Fe(II) in the ground state and 1% in the intervalence excited state. More recently, the spin density distribution in the ground state has been independently estimated from polarized neutron studies (Herren et al. 1980; Wills et al. 2005). In the series Rb$_2$Sb$_x$Sn$_{1-x}$Cl$_6$, the energy of the Sb(III,V) ground state in the undiluted system ($x=1$) was calculated to vary from 0.46 eV, below that of the Sb(IV,IV) excited state, down to 0.04 eV in a highly diluted system (Allen & Hush 1967). The reorganization energy remained constant at approximately 2.0 eV, indicating that vibronic coupling is predominantly due to internal modes of the hexachloride complex ions. The latter were identified by infrared and Raman spectroscopy (Barrowcliffe et al. 1967; Clark & Trumble 1976), practically unshifted from their energies in the corresponding single-valence species. Such compounds, like the Pt(II,IV) ones extensively investigated by

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Clark (Clark et al. 1976; Clark & Turtle 1978; Clark 1990) and further by Yamashita in this discussion (Takaishi & Yamashita 2008), are manifestations of deeply trapped charge density waves, in essence of ‘negative U’ (Anderson 1958; Clark & Turtle 1978; Clark 1990). A modified method for estimating $J$ due to Cave & Newton (1997), named the generalized Mulliken–Hush theory, has been proposed more recently and applied widely.

A topic of continuing interest, since the earliest models for mixed valence were put forward, is the distinction between localized and delocalized mixed-valence systems on the vibrational time scale (classes 2 and 3 in the generalized kinetic sense). The criterion for assigning a mixed-valence molecule or solid to one or the other is whether the adiabatic charge transfer energy is much greater or less than the inter-atomic resonance integral (Mayoh & Day 1972), or alternatively whether the ratio $2J/\lambda$ is less or greater than 1 (Hush 1975). However, in any particular case, the decision may not be easy to make. The first report of an intervalence band in an apparently symmetrical mixed-valence system, where both initial and final electronic states have equal energy, came from Creutz & Taube (1969). This was the iconic $[(\text{NH}_3)_5\text{Ru(pyrazine)}\text{Ru(NH}_3)_5]^{15+}$ ion, where each Ru has a formal +2.5 oxidation state. It is ironic that the correct description of the ground state of the Creutz–Taube ion remains controversial so many years later. It has been thought for some time that the correctness of a completely delocalized description on the vibrational time scale was validated by the smooth variation of intramolecular infrared frequencies as the charge on the ion increases from +4 to +5 and +6 (Beattie et al. 1976; Best et al. 1989) and by the demonstration that the excited intervalence state had zero dipole moment (Oh et al. 1991). However, quite recently, Demadis et al. (2001) presented compelling evidence that many mixed-valence ions may be regarded as occupying the class 2–3 borderline and suggested that the Creutz–Taube ion may also be so described (Concepcion et al. 2008). The evidence in question is the occurrence of weak symmetric modes in the infrared spectrum (Furholz et al. 1984) and weak asymmetric modes in the resonance Raman spectrum (Lu et al. 1995). Until recently, it has not been possible to estimate $\lambda$ for a delocalized system, but a method for doing so applied to the Creutz–Taube ion establishes that indeed the ion is extremely close to the $2J=\lambda$ borderline and is thus assignable to the borderline mixed 2–3 class. The implications of this for vibronic structure and other properties of 2–3 systems are evidently quite profound, and are currently being investigated (D’Alessandro & Keene 2006). Among novel coordination complexes are further examples straddling this borderline (Bursten et al. 2002), some of which are described in this discussion by Chisholm (2008).

Theory has advanced rapidly, hence only a few salient points will be noted here. Piepho et al. (1978) showed how to extend the theory of intervalence absorption to include coupling to many asymmetric vibrational modes, with a corresponding detailed account of temperature dependence. This was applied successfully to the mixed-valence $\text{M}_2\text{SbCl}_6$ systems by Prassides & Day (1984). The importance of symmetric modes (neglected in the Piepho–Krausz–Schatz approach) has been stressed (Hush 1982; Reimers & Hush 2004; Reimers et al. 2008); these modes becomes critical as $J$ increases. In modelling the intervalence band envelopes of photosynthetic dimer cations, 50 symmetric and 20 asymmetric modes are involved (Reimers et al. 2005). Theoretical
calculations of structure, excited states and response properties must be carried out at a very high quantum chemical level, and the environment (protein, solution, crystal, etc.) has to be included from the start (Reimers et al. 2005): these calculations are typically highly demanding in computer time, although this is alleviated by careful use of density functional theory. In this discussion, Kubiak and colleagues point out the crucial importance of the solvent environment (Glover et al. 2008).

There is much corresponding innovation on the experimental side in investigating mixed-valence systems. The use of resonance Raman spectroscopy for probing intervalence phenomena by Zink and Nelsen (Lockard et al. 2006) using the Heller approach, complementing earlier work by Clark on mixed-valence platinum and other systems (Clark & Dines 1986), is yielding highly detailed information about the electronic structure and partition of the reorganization energy in a variety of molecular complexes. Barbara’s investigations of intervalence absorption of both ground and excited states using femto-second spectroscopy (Reid et al. 1995) takes us into a new and fascinating time-domain, with concomitant questions arising concerning the definition of localization and refinement of the concept (see also Lu et al. 1995). In the present meeting, Boxer also discusses the use of Stark spectroscopy to probe IT transitions in systems near the class 2/3 borderline (Silverman et al. 2008).

The study of thermal electron transfer kinetics in solution has prompted the synthesis of a great variety of mixed-valence ions in which donor and acceptor groups are linked through a ligand bridge. One of the most interesting discoveries by Paddon-Row (2003) has been that, contrary to intuition, a very rapid electron transfer can take place either thermally or photochemically through saturated alkane-type bridges. Many rigid systems of this type with bridges up to 20 Å in length have been prepared and their properties interpreted through photoelectron studies of delocalization and by the study of intervalence bands. The phenomenon is well understood theoretically and is of the highest importance for understanding the mechanisms of electron transfer through proteins. This is in contrast to the photosynthetic mixed-valence dimer cations, where there is no such link. Another issue, also arising in some metal-containing biological systems, is what happens when the bridging group is not electronically ‘innocent’ (Jorgensen 1969), a wider issue taken up by Wieghardt (Ray et al. 2007).

Many mixed-valence compounds are not oligomeric coordination complexes but continuous lattice solids. In that case, knowledge gained from studies on finite clusters of mixed-valence metal atoms should, in principle, be capable of being extended to the infinite lattice. Questions such as those discussed above about the extent of delocalization occur for ionic solids where a change of electrical properties from insulating to metallic takes place via a Mott transition. As in Mott’s original derivation (Mott 1990, 1987) for an atomic hydrogen lattice, this is often thought of as a consequence of competition between electron repulsion and orbital overlap. However, Larsson has convincingly argued that electron–phonon coupling is crucial, being evidently of the same kind as that encountered in the theory of isolated mixed-valence systems, and he has recently put this on a firm theoretical footing (Larsson 2006, 2008). More generally, wherever polaron motion is discussed in condensed matter physics, there is a close analogy with the vibronic coupling effects identified in chemical mixed-valence systems. The concept of mixed
valence extends beyond the partly filled d-shells of the transition metals and in this discussion, Rosseinsky and colleagues describe chemical doping of a purely Main Group system (Fogg et al. 2008). Similarly, Prassides et al. (2008) discuss an unusual situation occurring in a 4f system, where the anions are fulleride clusters, which are also redox-active. Of course, not only electrical but also magnetic properties are determined by the analogues of $J$ and $\lambda$. Prussian blue, perhaps the best-known mixed-valence solid, becomes magnetically ordered even though the high-spin Fe(III) ions are separated by 10 Å or more owing to a finite $J$ and, remarkably, it is a ferromagnet (Ludi & Guedel 1973). In such a class 2 mixed-valence system, the ferromagnetic exchange is neatly explained in a Heitler-London formalism as being due to admixture of the intervalence excited configuration into the ground state (Mayoh & Day 1976). This presages much later work on molecular magnets.

Since the unusual magnetic behaviour of Prussian blue first came to light nearly 40 years ago, many analogues containing other metals have been synthesized, some with ordering temperatures higher than 300 K. Recent progress in that field is surveyed by Verdaguer and colleagues in this discussion (Herrera et al. 2008). Likewise, finite class 2 clusters containing Mn(II) and Mn(III), for example, have combinations of ferro- and antiferromagnetic intra-cluster magnetic exchange, which yield very high spin ground states so that the clusters behave as nano-sized superparamagnets, as described here by Christou (Stamatatos & Christou 2008). When analogous situations are found in infinite lattice oxides, such as perovskites, we find many fascinating phenomena arising from the different distributions of the two oxidation states, coupled with the interaction between localized and delocalized electrons. The latter gives rise to the property of ‘colossal magneto-resistance’, as Raveau (2008) and Shenoy & Rao (2008) reveal in this discussion.

Certain mixed-valence complexes continue to be of great interest as vitally important pigments in artwork (manuscripts, paintings, postage stamps, frescoes, etc.), notably Prussian blue (class 2), in which the chromophore is Fe(II/III), and lazurite (ultramarine blue, Na₈[Al₆Si₆O₂₄]Sn, class 2/3), in which the key chromophore is $S_{3\text{-}}$ (Clark & Franks 1975; Clark 1984). Moreover, many others such as Fe₂O₃, Fe₃O₄, Pb₂O₄ and Mn₃O₄ have long been used as pigments in ceramics and other forms of artwork (Best et al. 1995; Smith & Clark 2004; Clark 1995, 2007).

To conclude this brief overview, the last 40 years have seen huge strides in understanding the subtle interplay between electronic exchange, electron repulsion and electron–phonon interaction that come into play when atoms of differing oxidation state and environment are brought together either in finite clusters or infinite lattices. At the same time, unexpected new phenomena, such as high temperature superconductivity and colossal magneto-resistance, have emerged to challenge both our understanding and our experimental techniques. There is no doubt that mixed valence retains the fascination it had when first recognized as a distinct segment of chemistry. It is to be hoped that this discussion gives a comprehensive picture of the present state of play, while identifying areas where understanding remains incomplete.

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References


Burns, R. G. 1970 Mineralogical applications of crystal field theory. Cambridge, UK: Cambridge University Press.

Bursten, B. E., Chisholm, M. H., Clark, R. J. H., Firth, S., Hadad, C. M., MacIntosh, A. M., Wilson, P. J., Woodward, P. M. & Zaleski, J. M. 2002 Oxalate-bridged complexes of dimolybdenum and ditungsten supported by pivalate ligands: \((\text{BuCO}_2)_3\text{M}_2(\mu-O_2\text{CCO}_2)\cdot\text{M}_2(O_2\text{C}^\text{Bu})_3\). Correlation of the solid-state, molecular, and electronic structures with Raman, resonance Raman, and electronic spectral data. J. Am. Chem. Soc. 124, 3050–3063. (doi:10.1021/ja011786j)


Clark, R. J. H., Franks, M. L. & Trumble, W. R. 1976 Resonance Raman spectra and excitation profiles of the mixed valence compound Wolfram’s red \([\text{Pt}^{\text{III}}(\text{C}_2\text{H}_3\text{NH}_2)_4]_2[\text{Pt}^{\text{IV}}(\text{C}_2\text{H}_3\text{NH}_2)_4\cdot\text{Cl}_2]\cdot\text{Cl}_4\text{H}_2\text{O}\). Chem. Phys. Lett. 41, 287–292. (doi:10.1016/0009-2614(76)80812-3)


