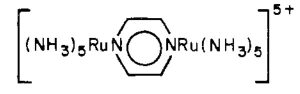
# Correspondence

## Electron Delocalization in the Mixed-Valence $\mu$-Pyrazine-decaamminediruthenium(5+) Ion[1a]

AIC507514

*Sir:*

The $\mu$-pyrazine-decaamminediruthenium(5+) ion I, which



I

is formally a Ru(II)–Ru(III) mixed-valence complex, was first described by Creutz and Taube.[2] This has stimulated interest in the preparation of mixed-valence compounds of bifunctional ligands, the physical properties of which provide data which are useful for further development of electron-transfer theory. However, the question of the electronic structure of this ion, although much discussed, has not yet been resolved.

An ion such as I can have either a symmetrical or an unsymmetrical ground state. In the former case, the complex will have a symmetrical delocalized electronic ground state. In the latter case, the complex would be of the weak-interaction type,[3] in which the hole in the $4d^6$ subshell is approximately described as trapped at one Ru center. As there would then be two states of equal energy, the hole (or electron) would transfer thermally between two potential wells of equal depth and exhibit a multiphonon intervalence transfer[4,5] absorption band characteristic of weak-interaction complexes. In reality, the two equivalent-hole states would each be partially delocalized over the ligand system.

Creutz and Taube initially proposed a weak-interaction (trapped-valence) ground state for the ion I. An absorption band observed in the infrared spectrum in $D_2O$ solution at 0.79 eV (6400 $cm^{-1}$) was assigned to an intervalence-transfer band. They applied the theory of Hush[4,5] which relates optical and thermal electron-transfer probabilities in such compounds and concluded that the intramolecular transfer rate at 300 K was of the order of $10^9$ $s^{-1}$. In subsequent work,[6] it has also been suggested that chemical properties of the complex are more consistent with a weak-interaction than with a delocalized ground state. However, it is clear that this can only be resolved by measurement of physical properties. Some of these that have been made (e.g., proton NMR measurements[7]) would be consistent with either description, and others (e.g., Mössbauer measurements[8]) are not yet sufficiently precise to be interpreted with confidence. In discussing this question, we concentrate here in turn on three types of physical measurement which are of central importance. These are (i) analysis of the near-infrared "mixed-valence" absorption band and of its temperature dependence, (ii) the infrared vibrational spectrum, and (iii) the x-ray photoelectron (ESCA) spectrum.

**(i) The Near-Infrared "Mixed-Valence" Band.** If the ion had an unsymmetrical ground state, the band with a maximum at 0.79 eV ($D_2O$) would most naturally be assigned to an intervalence transfer transition;[4,5] this is a multiphonon transition in which, in terms of a single effective phonon frequency $\bar{\omega}$

$$h\nu_{\max} = S\hbar\bar{\omega} \qquad (1)$$

where $S$ quanta are excited. The quantity $S\hbar\bar{\omega}$ is also equal to the electron–phonon (or electronic–vibrational) coupling energy $\chi$. If the electronic coupling integral between the two quasi-localized states is $J$, then the high-temperature activation energy for intramolecular electron transfer would be $(\chi/4) - J$ on this model. However, such an assignment is not compatible with the shape of the band envelope for the transition for a multiphonon intervalence transfer. In particular the half-width (and hence the second moment)[4,5] is far too small to be compatible with this without modification to the theory. The relatively narrow bandwidth immediately suggests, in fact, a delocalized rather than a localized ground state. For a delocalized ground state, assuming as above linear electron–phonon coupling with a single effective frequency $\bar{\omega}$, the half-width $\Delta\nu_{1/2}$ of the lowest bonding–antibonding transition can be calculated from potential energy functions given elsewhere[9] as

$$\Delta\nu_{1/2} = \hbar\bar{\omega}(4 \ln 2)^{1/2}\theta(1-\theta)^{-1/2} \coth\left(\hbar\bar{\omega}(1-\theta)^{1/2}/2kT\right) \qquad (2)$$

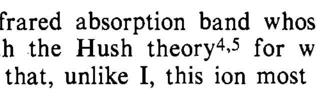
where $\theta = \chi/2J$.

The spectrum of the near-infrared band of the pentabromide of I has been studied[10] in the solid state by diffuse reflectance over the temperature range 4–400 K. The temperature variation of the second moment conforms within experimental error with eq 2. The maximum frequency on this interpretation is given by

$$h\nu_{\max} = 2J \qquad (3)$$

Analysis of the data leads to the following values for the pentabromide: $J = 0.39$ eV, $\chi = 0.48$ eV, $\hbar\bar{\omega} = 800$ $cm^{-1}$. The features of the absorption band can thus be accounted for in a self-consistent way. We note further that the solution band maximum is very insensitive to the nature of the solvent ($2 \times 10^{-2}$-eV shift over a very wide range of solvent polarity[6]) and is almost identical (again within $2 \times 10^{-2}$ eV) with that in the solid. This strongly suggests that the charge density distribution is symmetrical and essentially the same in ground and excited states, as would be expected for a delocalized complex. This insensitivity to environment is in marked contrast to the expected quite large shifts found for other complexes which are believed to have trapped-valence (weak-interaction) ground states.[11]

It is interesting to note that the related mixed-valence pyrazine complex II has recently been found[12] to exhibit a



II

broad near-infrared absorption band whose half-width is consistent with the Hush theory[4,5] for weak-interaction complexes, so that, unlike I, this ion most probably has a trapped-valence ground state.

**(ii) Vibrational Spectra.** Complex I was first isolated[1] in the solid state as a tosylate salt, and infrared spectra obtained were difficult to interpret owing to superposition of bands due to the organic anion. To eliminate this problem, the bromide salt of I, the 5+ ion, together with the bromide salt of the corresponding Ru(III)–Ru(III) 6+ and the tetrabromozincate of Ru(II)–Ru(II) 4+ complexes were prepared. It was found[10] that ir bands attributable to the 5+ complex I were not superpositions of corresponding bands of the 4+ and 6+ complexes. Where bands of I were measurable, a single band was found at a position intermediate between the corresponding bands of the 4+ and 6+ complexes. An $NH_3$ "rocking" frequency ($\rho_{NH_3}$) of 800 $cm^{-1}$ was found for the 5+ complex; the corresponding frequencies for the 4+ and 6+ complexes were 750 and 840 $cm^{-1}$ respectively. Similarly, a stretching frequency ($\nu_{Ru-NH_3}$) attributed qualitatively to a metal–$NH_3$ stretching mode was found at 449 $cm^{-1}$ for the 5+ ion, while the corresponding frequencies for the 4+ and 6+ ions were 438 and 461 $cm^{-1}$, respectively. Taube et al.[6] also measured some ir bands of some simple salts of I; they noted that bands obtained for the 5+ complex were "rather intermediate" between those of 4+ and 6+ ions and found no evidence of superposition of 4+ and 6+ bands in the 5+ spectra.

The simplest conclusion from these results is that the ion I has a delocalized, symmetrical ground state. This agrees with the interpretation of the near-infrared "mixed-valence" band.

**(iii) X-Ray Photoelectron Spectra.** The XP spectra of the tosylate salts of I and of the corresponding 4+ and 6+ ions have been reported by Citrin.[13] Although the Ru 3d spectrum is partially obscured by the strong C 1s ionization, the XP spectrum of I is analyzed as showing two $3d_{5/2}$ bands separated by 2.7 eV, at positions roughly corresponding to those in the Ru(II)–Ru(II) and Ru(III)–Ru(III) complexes, respectively. This was interpreted[13] as providing direct evidence that the ion I contains two different Ru centers (i.e., Ru(II) and Ru(III)) in the ground state. It has generally been assumed that a mixed-valence complex would show only one XPS band at a position intermediate between those of the (II) and (III) ions if it possessed a delocalized ground state. However, it has recently been shown[9] that for a delocalized complex of the type of I, with $J \simeq 0.4$ eV, two $3d_{5/2}$ bands would be expected at energies very close to those of the (II) and (III) ions. The reason for this somewhat surprising result is that such complexes are highly polarizable, and the photoionized valence states are split owing to electron relaxation in the strong field of the core vacancy. We may conclude from this that the XPS measurements, at least at their present level of resolution, provide no evidence against the assignment of a delocalized ground state to I. Quantitative predictions have been made[9] of the rather small departures expected in frequency and intensity from localized behavior, and very accurate future XPS measurements may possibly further test the assignment.

Although the assignment of a delocalized ground state to the ion I runs counter to the generally accepted view, we believe that it is the one in best accord with the available physical measurements.[14] It should be mentioned finally that Mayoh and Day[15] have argued in favor of the opposite interpretation (trapped-valence ground state) by proposing a criterion for delocalization based on perturbation theory. This assumes that $J$ should be less than $\chi/4$, in our terminology, for the lower potential surface to contain only one minimum. As pointed out elsewhere,[9] this criterion for the existence of a single minimum is incorrect (it should be $J < \chi/2$), but in any case the use of perturbation theory to obtain the ground-state electronic wave function is also incorrect when the electronic coupling is large. The interpretation of the wave function of mixed-valence complexes proposed by Mayoh and Day has no physical basis. Their further perturbation calculations[16] on the metal–ligand charge-transfer band of I, based on the assumption of a trapped-valence ground state, are not relevant to a delocalized complex.

Further details of the measurements and calculations reported above, and discussion of the factors influencing electron delocalization, will be published shortly.

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## Further Investigations Concerning the Existence of Complexes of Lithium Aluminum Hydride and Aluminum Hydride in Diethyl Ether and in the Solid State

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*Sir:*

Recently[1] we reported a study of the reaction of $LiAlH_4$ and $AlH_3$ in several mole ratios in diethyl ether and THF in an attempt to prepare the previously reported compounds $LiAl_2H_7$, $LiAl_3H_{10}$, and $LiAl_4H_{13}$. Contrary to previous reports no evidence was found to indicate the existence of any of the above compounds or any complex between $LiAlH_4$ and $AlH_3$. However, while the above report was in press, we found what could be interpreted as some evidence[7] possibly indicating the existence of $LiAl_2H_7$ when prepared according to eq 1 and 2. We have now studied the reaction of $LiAlH_4$ and LiH with $AlCl_3$ in detail as possible routes to $LiAl_2H_7$ as well as $LiAl_3H_{10}$ and $LiAl_4H_{13}$.

$$7LiAlH_4 + AlCl_3 \xrightarrow[0\ ^\circ C]{Et_2O} 4LiAl_2H_7 + 3LiCl \qquad (1)$$

$$7LiH + 2AlCl_3 \xrightarrow[-13\ ^\circ C]{Et_2O} LiAl_2H_7 + 6LiCl \qquad (2)$$

The reaction of $LiAlH_4$ and $AlCl_3$ in 7:1 molar ratio in diethyl ether at 0 °C (eq 1) yields a white precipitate of lithium chloride and a clear solution containing $LiAlH_4$ and $AlH_3$ in equimolar portions. The presence of $LiAlH_4$ and $AlH_3$ in solution is confirmed by the occurrence of characteristic strong bands at 1785 $cm^{-1}$ (Al–H stretching vibration in $AlH_3$) and 1760 $cm^{-1}$ (Al–H stretching vibration in $LiAlH_4$). The elemental analysis of the white solid isolated after complete removal of the ether solvent showed a Li:Al:H ratio of 0.571:1.00:3.33. Anal. Calcd for "$LiAl_2H_7$"·$0.29Et_2O$:[8] Li,