Mixed-valence Interaction in η^7-Cycloheptatrienylmolybdenum Complexes

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Summary Electronic absorption and *X*-ray photo-electron spectroscopy studies indicate that the complexes $[Mo_2(\mu\text{-}X_3)(\eta^7\text{-}C_7H_7)_2]$ (X = Cl, Br, or I) are mixed-valence compounds possessing an unsymmetrical ground state.

RECENTLY reported η^7-cycloheptatrienyldimolybdenum complexes $[Mo_2(\mu\text{-}X_3)(\eta^7\text{-}C_7H_7)_2]$ (X = Cl, Br, or I)[1] may possess either an unsymmetrical ground state in which the vacancy in the 4*d* sub-shell is trapped on one molybdenum centre, or a symmetrical ground state with strong metal–metal interaction and complete delocalization of charge. Electronic absorption and *X*-ray photo-electron spectral measurements are consistent with a trapped mixed-valence ground state involving weak metal–metal interaction.

The electronic absorption spectra recorded by diffuse reflectance show that the three complexes absorb strongly in the near i.r. region. This feature is not present in the spectra of the tetrafluoroborate and hexafluorophosphate salts of $[Mo_2(\mu\text{-}X_3)(\eta^7\text{-}C_7H_7)_2]^+$ (X = Cl, Br, or I). As expected for an intervalence transfer transition, the position of the absorption maxima in the neutral complexes depends on the bridging halide (X = Cl, at 1·3 eV; X = Br, at 0·9 eV). The band shape closely resembles those reported for weak-interaction complexes.[2] The *X*-ray photo-electron spectra (Vacuum Generators ESCA 2 spectrometer, Al–K$_\alpha$ radiation, samples with particle size $< 50\,\mu$m on gold plated stainless steel mesh) were measured relative to the gold $4f_{7/2}$ line at 84·0 eV. The spectra in the molybdenum

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$3d$ region showed two sets of $3d_{5/2}$ and of $3d_{3/2}$ bands separated by $3{\cdot}0 \pm 0{\cdot}2$ (X = Cl), $2{\cdot}5 \pm 0{\cdot}2$ (X = Br), and $2{\cdot}0 \pm 0{\cdot}2$ (X = I) eV. The lowest binding energy component of the composite photo-electron signals coincided with the $3d_{5/2}$ peak observed for $[\mathrm{MoI(CO)_2(\eta^7\text{-}C_7H_7)}]$ at $229{\cdot}1 \pm 0{\cdot}2$ eV.

We have also measured the Mo $3d_{5/2}$ signal in $[\mathrm{Mo(CO)_3(\eta^6\text{-}C_7H_8)}]$ at $228{\cdot}5 \pm 0{\cdot}2$ eV in close agreement with a previously reported value.[3] A binding energy shift of 1 eV has been shown to produce a variation in charge of *ca.* 0·3 units.[3,4] Moreover, if the latter complexes can be considered as typical of $\mathrm{Mo^0}$ systems then those studied here may be best designated as $\mathrm{Mo^0}$–$\mathrm{Mo^I}$ mixed-valence complexes

Similar d^6 and d^5 complexes occur for ruthenium. Thus binuclear $\mathrm{Ru^{II}}$–$\mathrm{Ru^{III}}$ complexes with localised (unsymmetrical) and delocalised (symmetrical) ground states have been reported.[5] For systems of this kind, however, it has been noted that data from *X*-ray photo-electron spectroscopy may not always unequivocably identify the nature of the ground state in mixed-valence complexes.[6] Although such compounds possessing a delocalised ground state might be expected to show only one set of bands in the *X*-ray photo-electron spectrum it has been demonstrated that such complexes could have two accessible unsymmetrical excited states owing to electron relaxation in the strong field of the core hole. Notwithstanding this, however further insight into the nature of the system under consideration may be gained from the shape of the electronic absorption band in the near-i.r. spectral region. Here the presence of a relatively broad absorption taken together with the *X*-ray photo-electron measurements of the molybdenum complexes indicates a localised trapped-valence ground state. The spectroscopic data also indicate that the properties of the mixed-valence electron transfer transition between the $\mathrm{Mo^0}$ and $\mathrm{Mo^I}$ atoms are dependant upon the bridging ligand. The extent of metal–metal interaction and rates of thermal electron transfer between the metal centres can therefore be controlled by systematically varying the ligands.

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