Excited-State Mixed Valence in Transition Metal Complexes

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Mixed valence in the lowest-energy metal-to-ligand charge-transfer excited state of di-(4-acetylpyridine)tetraammineruthenium(II) complexes is defined and analyzed. The excited state has two interchangeably equivalent ligands with different oxidation states. The electronic absorption band energies, selection rules, and bandwidths are analyzed quantitatively in terms of the signs and orientations of the transition dipole moments, sign and magnitude of the coupling, and resonance Raman analysis of displaced normal modes.

Scheme 1

mono   trans   cis

Excited-state mixed valence (ESMV) occurs when an excited electronic state has two or more interchangeably equivalent sites with different formal oxidation states.[1-4] For example, in metal-to-ligand charge transfer, excitation transfers the electron from an orbital primarily metal d in character to empty orbitals on the identical ligands. In the absence of coupling between the ligands, one electronic absorption band would be observed because the transition energies would be identical, and in the excited state, the electron could be thought of as occupying an orbital on either of the ligands. This situation is reminiscent of a Class 1 ground-state mixed-valence compound.[5] If coupling occurs, the excited state and spectroscopic features become more complex. The spectroscopic consequences were first treated quantitatively in organic hydrazine complexes where the ESMV absorption bands are well separated in energy from other absorption bands in the molecule.[1-4] ESMV is common in the charge-transfer excited states of metal complexes that contain two (or more) identical ligands. It is difficult to find unobscured examples of ESMV in transition metal complexes because ligand field transitions, intraligand transitions, and the desired
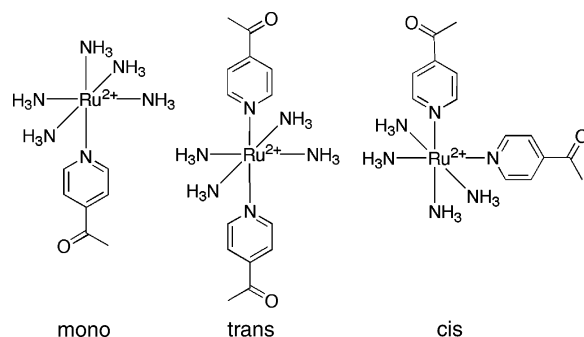
ESMV transitions often overlap. In this Communication, we report and analyze ESMV in the di-(4-acetylpyridine)-tetraammineruthenium(II) hexafluorophosphate complexes shown in Scheme 1,[6-11] where the ruthenium-to-substituted pyridine charge transfer is lower in energy than and well separated from the d—d and intraligand absorption bands. The most important absorption spectroscopic signature of a mixed-valence excited state is the presence of two bands separated in energy by one-half of the effective coupling. The angle between the transition dipole moments and the sign of the coupling determine the relative absorptivities of the two bands and also if the high- or low-energy band is the most intense. These factors have not been analyzed for transition metal complexes. The orientation of the transition dipole moments can be varied in the complexes in Scheme 1; they are antiparallel in the trans complexes and at right angles to each other (with equal contributions of parallel and antiparallel transition dipoles) in the cis complex. The sign of the coupling (which is normally not important in ground-state intervalence spectroscopy) is critical in determining the selection rules in the ESMV spectrum.

The lowest-energy absorption bands of the complexes in Scheme 1 have been assigned to the MLCT transitions.[8-11] The spectra contain the features expected for an ESMV

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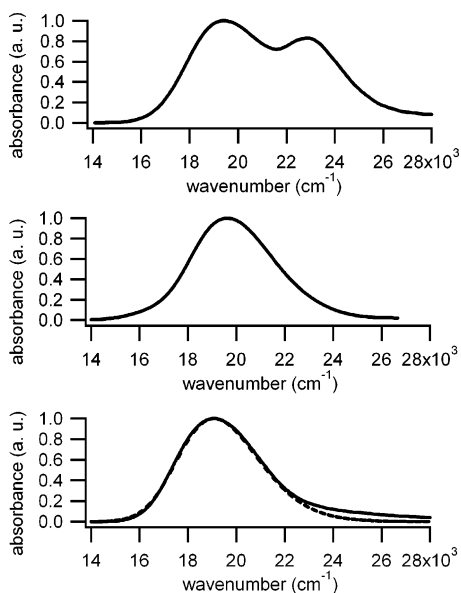
Figure 1. Electronic absorption spectra in butyronitrile solution at 295 K: (top) cis complex, (middle) mono complex, and (bottom, solid line) trans complex. The broken line is the calculated absorption spectrum based on the Raman displacements.
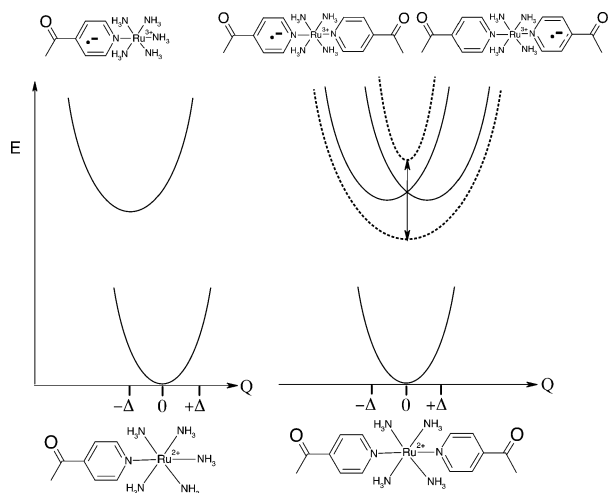

Figure 2. Ground-state and excited-state potential energy surfaces for the mono complex (left) and the trans complex (right). The solid upper lines represent the excited-state diabatic surfaces in which an electron is either on one ligand or the other. The broken lines represent adiabatic surfaces. The arrow shows the splitting caused by coupling.

interaction (Figure 1). The monosubstituted complex exhibits one band (19 650 cm^{-1}), and the cis complex exhibits two bands of similar intensities (at 19 420 and 22 830 cm^{-1}). However, the spectrum of the trans complex contains one band at 19 050 cm^{-1} and a weak shoulder at lower energy. These differences are predicted by the excited-state mixed-valence model as discussed below.

The simplest treatment of the ESMV spectra is based on the potential-energy surfaces shown in Figure 2.[1–4]

Upon absorption of a photon, charge transfer occurs from the ruthenium center to one of the 4-acetylpyridine ligands, leaving the ruthenium with a formal charge of +3 and the ligand with a charge of −1. In the two di-(4-acetylpyridine) complexes, charge transfer to either of the two symmetrically equivalent pyridine ligands occurs with equal probability and

energy. To assist the comparison of the cis and trans ESMV complexes, a similar complex that does not exhibit ESMV, the mono-(4-acetylpyridine) complex will first be described. A potential energy surface with a minima at $Q = 0$ represents the ground state with the ruthenium in a divalent oxidation state and a neutral 4-acetylpyridine ligand. The mono-(4-acetylpyridine) complex requires only one upper potential-energy surface for the charge-transfer state described above. A transition from the ground state to the upper displaced state produces one band in the visible part of the absorption spectrum (19 650 cm^{-1}, see Figure 1).

For the cis and trans complexes, the ground-state PE surface has its minimum at $Q = 0$, representing the symmetric charge distribution with both 4-acetylpyridine ligands being formally neutral and the ruthenium being in its divalent oxidation state. Upon electron transfer from a ruthenium d orbital to one of the ligand $\pi*$ orbitals, the molecule exists in an asymmetric excited state. In this diabatic (uncoupled) regime, two upper excited-state surfaces are needed to represent the electron on one or the other of the two ligands. The surfaces are displaced by $-\Delta Q$ and $+\Delta Q$ along an asymmetric coordinate, and both are equal in energy at $Q = 0$.

In the uncoupled regime, only one band occurs in the absorption spectrum. Coupling between these two surfaces yields two adiabatic surfaces shown by the broken lines in Figure 2 , which have zero slopes and different energies at $Q = 0$. This splitting yields two bands in the absorption spectrum of the di-(4-acetylpyridine) complexes. The energy difference between these two adiabatic surfaces is equal to the energy difference between the two bands in the absorption spectrum and is related to the strength of the coupling. The energy difference is 3400 cm^{-1} for the cis complex.

The selection rules are governed by the orientation of the transition dipoles and the sign of the coupling.[1–4] For the trans complex, the transition dipoles are antiparallel, and in the diabatic basis, they are equivalent in magnitude but opposite in sign. In the adiabatic basis, one transition is dipole allowed, and the other is vibronically allowed but dipole forbidden.[6] If the sign of the coupling is positive, the transition to the lowest-energy state is allowed and vice versa. The sign of coupling can be deduced from a neighboring orbital model using simple molecular orbital theory.[2,12,13]

A molecular orbital description of the compounds shows that the out-of-phase combination of pyridine orbitals is the most stable combination.[6] The effective coupling is thus positive, and the lowest-energy ESMV band is allowed, as observed in the absorption spectrum of the trans complex.

For the cis complex, the transition dipoles are at 90°, and the observed spectrum is a superposition of the parallel and antiparallel components. Thus two bands are observed in the absorption spectrum.

The bandwidths in the absorption spectrum are dominated by distortions in the symmetric normal coordinates of

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Table 1. Experimental and Calculated Raman Data for the trans Complex

mode (cm^{-1})	calcd (cm^{-1})[a]	I_k/I_k[b]	Δ[c]	assignment
395	385	1.69	1.02	Ru−N (NH$_3$) stretch
430		0.74	0.61	
560	595	0.44	0.37	ring distortion in plane with Ru−N (NH$_3$) stretch
598	614	0.76	0.45	H−N−H bend
755	763	1.98	0.59	in-plane C−C−C and C−N−C bend, Ru−N(py), C(py)-C(carbonyl)
859	877	2.69	0.60	H−C out of plane wag
967	983	1.45	0.33	C=C in plane with Me−H wag
1026	1022	2.78	0.51	C−N−C and Ru−N (py) stretch
1095	1120	1.67	0.37	C=C in-plane stretch
1209	1245	8.99	0.77	C=N, C=C stretch, and H−CC−H in-plane wag
1279	1284	3.25	0.37	C=C in-plane stretch
1494	1488	1.42	0.21	H−CC−H in-plane wag with C=C stretch
1546	1580	0.84	0.16	C=O, C=N, and C=C stretches
1606	1639	19.45	0.86	ring elongation about C=C with C(py)−C(carbonyl) stretch
1686	1678	4.07	0.32	C=O stretch

[a] Calculated at B3LYP/LANL2DZ. [b] Intensities relative to KNO$_3$ internal standard. [c] Dimensionless distortions.

vibration. The symmetric modes can be probed by resonance Raman spectroscopy. Resonance Raman intensities are used to calculate the displacements of the excited-state potentials along the symmetric coordinates.[14−22]

The Raman spectrum of the trans complex contains fifteen vibrational modes in the range between 250 and 2000 cm^{-1}, with an intensity greater than 2% of that of the most intense signal. These modes were assigned by comparison with the literature[23] and those calculated by DFT in Gaussian[24] (see Table 1). In the region from 1000 to 1700 cm^{-1}, 4-acetylpy-

ridine ligand vibrations dominate the spectrum. All of these ligand modes show resonant enhancement, but the two modes at 1604 and 1210 cm^{-1}, corresponding to the intraligand distortions are substantially more enhanced than the others. These modes involve C=C and C=N displacements that are expected to undergo large distortions when promoting an electron into the π* antibonding orbital of the pyridine ring. The most enhanced mode, at 395 cm^{-1}, corresponds to a symmetric stretch of the ruthenium−nitrogen (amine) bonds. The transfer of an electron from the metal center to the pyridine ligand formally oxidizes the ruthenium to its trivalent state. The ruthenium-localized oxidation has the greatest impact on the bond lengths of those ligands coordinated to it with greatest electrostatic nature.[25] In this case, the amine−ruthenium bonds are the most electrostatic (over the pyridines), and the corresponding vibration is the most enhanced. This observation is consistent with the crystallographic data for the Creutz−Taube ion, in which an oxidation from Ru(II) to Ru(III) has little effect on the ruthenium−pyrazine bond length but reduces those of the ruthenium−amine bonds.[25]

To obtain more quantitative information about the distortion of the metal−amine bond in the excited state, the absolute magnitudes of the distortions were calculated. The ratios of the distortions are found from the intensities in the resonance Raman spectra, and the individual dimensionless distortions for the normal modes are calculated (except for the sign) from the relationship between them and the absorption bandwidth.[16,17] The distortions for each individual bond (in angstroms) are calculated using the relationship between the normal and symmetry coordinates and the reduced mass. The calculated value for the Ru−amine bond length change in the 395 cm^{-1} mode is 0.031 Å. This calculated value for the Ru−amine bond length change is similar to that obtained from the crystallographic data for the Creutz−Taube ion, where the difference in the average of the ruthenium−amine bond length in its ruthenium(II) and (III) oxidation states is 0.036 Å.[25] The ruthenium−amine and C=C, C=N ligand modes are the most affected by the ESMV.

Excited-state mixed valence in metal complexes is expected to be a common phenomenon. The complexes presented here are unusual because the consequences of ESMV are clearly visible. The sign of the coupling mediated by the metal bridge is positive using the neighboring orbital model. The ruthenium−amine and the intrapyridine modes are most enhanced and confirm the nature of the transitions as MLCT.

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