DOE/ER/13809--T1

PERFORMANCE REPORT

INVESTIGATIONS OF CHARGE-SEPARATION PROCESSES IN METAL COMPLEXES

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Grant: DE-FG06-87ER13809
February 18, 1991

DOE/ER/13809--T1

DE92 004327

SUMMARY OF PROGRESS

The major thrust of the research has been the quantification of the excited states of inorganic complexes that display potential for mediating charge-separation processes. Investigations of copper(I) mixed-ligand complexes have been completed. Non-equilibrated emitting states have been assigned. Chemical tuning of the emission energy by modifying the basicity of the donor ligand on the metal has been achieved. Structure-property relationships have been defined for crystalline complexes of zinc containing both diimine and monothiol ligands. Correlation of the spectral shifts with the rotations of the thiol phenyl rings in different crystal phases has been shown by comparing with extended Huckel calculations and x-ray structures. Complexes of zinc containing diimine and dithiol ligands are shown to be polynuclear species. A trinuclear species can be forced to assume a binuclear structure by incorporating other non-coordinating ligands into the lattice. The transformation is accompanied by substantial photophysical changes. Syntheses and x-ray structure determinations of platinum(II) complexes containing diimine ligands only, both diimine and dithiol ligands, and dithiol ligands only have have been completed. An unusual platinum(III) bis(dithiol) species has been obtained and its structure determined. Investigations of the emission spectra of bis(bipyridine)platinum(II) have revealed the existence of multiple emitting states with both ligand-localized and charge-transfer characteristics.

COMPLETED PROJECTS

In previous annual progress reports we summarized the status of our investigations in three facets of the research: (a) assignment of the emitting levels of polypyridine complexes of copper(I) [1], (b) structure-property relationships occurring in $(nd)^{10}$ complexes [2-4], and (c) extended-Huckel calculations and their correlation with luminescence measurements on complexes displaying multiple phases. These results and preliminary work on some Pt(II) complexes are reported in several manuscripts that are in various stages of publication (abstracts are given here). Additional details of these studies will be reviewed in this report when they are related to the new work proposed.

CURRENT ACTIVITIES

Thermal Modulation Emission Spectroscopy [TME]

The TME method (described in previous progress reports and publications) has been used extensively in this laboratory to separate excited states of disparate orbital parentages and lifetimes. Because most of the phenomena interesting to us occur at temperatures below liquid N_2, however, the method became too expensive to be employed routinely. Thus, we have devised a new TME method that employs fiber optics for both excitation and detection [5]. The new design allows the TME experiment to be carried out directly in a liquid helium storage dewar, thus effecting considerable cost-savings. Temperatures from 4.2 K to 90 K can be attained and precisely maintained at the sample by raising and lowering the sample block inside the storage dewar. The apparatus can also be used to observe both steady-state and transient spectra. A modified sample holder that can accommodate several crystals or glasses is under contruction. This should lower our cryogenic fluid costs still further.

One limitation of the new technique is the UV cut-off limit for excitation that is controlled by the optical fiber composition, but this can be obviated with more expensive fibers (not currently needed for our studies). A second limitation is that sub-4.2K spectra cannot be obtained in this way since there is no way to pump on the helium. To obtain sub-4.2 K spectra we must resort to the previous (expensive) procedure of pumping on helium in a standard dewar.

The substantial cost-savings that can be achieved by recording spectra at low temperatures by this apparatus makes extensive measurements in the sub-77 K range feasible in our setting. Moreover, the temperature stability and control is within acceptable limits. With single photon counting the signal-to-noise ratio is also quite good. This technique and apparatus allow us to propose several new studies on metal complexes that can be accomplished within our budget.

Measurement of Zero-Field Splittings in Complexes

(a) Within the last year we have completed measurements of the zero-field splittings of several d^{10} complexes [6]. The method used was phosphorescence-microwave double resonance (PMDR). The intent of the study was to search for any interaction between the 'ligand-localized $\pi\pi^*$ triplet state' and the low-lying 'ligand-ligand charge-transfer' state. The complexes (listed in order of thiol substituent electron donating ability) were: $ZnCl_2(phen)$, $Zn(F_5\text{-}PhS)_2(phen)$, $Zn(4\text{-}Cl\text{-}PhS)_2(phen)$, and $Zn(4\text{-}CH_3\text{-}PhS)_2(phen)$. The results were conclusive: As the electron donating ability of the substituent increases, all three microwave transitions decrease and their decay rate constants increase. We have interpreted this result in terms of an increase in the mixing of the $\pi\pi^*$ and LLCT triplets and have estimated the extent of this delocalization.

To our knowledge this is the first quantitative assessment of this mixing to be made.

(b) We have also measured the zero-field splitting of the triplet LLCT manifold of the $Zn(4\text{-}CH_3O\text{-}PhS)_2(phen)$ complex (below 5 K)[7]. The measurements confirm the triplet assignment made previously in this laboratory [8]. Calculated splittings on the basis of a point charge approximation derived from MO's for benzene (HOMO) and 1,10-phenanthroline (LUMO) are much smaller than the experimental values for any reasonabl geometry of the complex. We suspect that the discrepancy can be traced to the neglect of the zinc ion orbitals in the donor molecular orbital of the LLCT configuration. These measurements are the first direct observations of the splittings of a LLCT emitting manifold. They are giving us information on the role of the metal ion orbitals in LLCT excited states.

(c) We have recently completed the measurement of the zero-field splittings of the emitting $^3\pi\pi^*$ manifold of the series of complexes ZnX_2(1,10-phenanthroline) where X = Cl, Br, I. These splittings will serve as a base-line for interpreting the splittings of highly-perturbed $^3\pi\pi^*$ levels that we plan to measure in the future.

Further Investigations of Structure-Property Relationships

(a) As reported previously, the d^{10} complexes of zinc manifest several crystal phases, each one exhibiting its characteristic emission spectra [2]. Recently, we have obtained a second phase of the $Zn(4\text{-}CH_3O\text{-}PhS)_2(phen)$ complex and subjected it to optical studies. In concert with the results from the first phase that we studied of this complex the new phase shows only LLCT emission, but there is both a short (nsec) and a long (msec) decay. We have determined the crystal structure and are pursuing further

measurements in search of the structural characteristics that produce no LLCT/$\pi\pi^*$ barrier in this complex and also a phase-dependent LLCT emission. The observation of the fast (10 nsec) decay component is strong evidence of singlet LLCT emission, our first indication that we may be able to measure the LLCT singlet-triplet splitting, a quantity that we very much desire. The S-T splitting would yield much information about the details of electronic charge distributions in these types of excited configurations.

(b) We have continued our structural and optical studies of complexes of the generic formula $[M(BS)_2(s\text{-phen})]$ and $[M(BS)_2(s\text{-bpy})]$ where s-phen is a substituted 1,10-phenanthroline, s-bpy a substituted bipyridine, BS an aromatic thiol, and M = Zn or Cd. Barriers are evident but no additional barrier parameters have been quantified. Considerable effort has been focussed on the $(4\text{-ClPhS})_2Zn(phen)$ complex since <u>two</u> ligand-localized triplets have been resolved. Their characteristics point toward factor-group splitting as the origin. [Traps cannot be conclusively ruled out]

(c) The extended-Huckel calculations on LLCT excited states have been continued. Our recent efforts have been directed toward explaining why the point-charge dipolar mechanism fails to account for the observed splittings of the LLCT triplet manifold.

(d) A convincing demonstration of the redistribution of the energy from the triplet $\pi\pi^*$ manifold to the LLCT manifold has been recorded. Both the <u>depopulation</u> of the former and the simultaneous <u>repopulation</u> of the latter have been shown. The evidence is unequivocal that the energy is being redistributed between the two orbitally disparate triplet manifolds by

heat pulses. We are currently attempting to measure the time-dependence of the emission profile as the redistribution occurs.

Charge-Transfer Intensity Model for Complexes

The question of the origin of the intensity of the prominent charge-transfer absorption bands that are characteristic of ruthenium(II) complexes with polypyridyl ligands and also of those displayed by copper(I) complexes with analogous ligands was investigated theoretically [9]. Mulliken's model for CT bands in simple A-B complexes [10-12] was extended to these d^6 and d^{10} complexes with symmetrically equivalent ligands. The theory was illustrated for a one-donor/two-acceptor complex in D_{2d} symmetry. The model correctly predicts the known symmetries of the prominent visible bands of $Cu(phen)_2^+$ and throws considerable light on the origin of the intense CT bands in asymmetric complexes of both d^{10} and d^6 configurations as well. It also rationalizes the observed intensity ratios between analogous CT bands in mono(diimine) and bis-(diimine) complexes of these types.

Preliminary Investigations of Platinum(II) Complexes

Because of the long-standing interest of this laboratory in d^8 complexes [13-15] and their excited states, we have synthesized and examined the electronic spectra of platinum(II) systems having diimine and/or dithiolate ligands. We have also determined the structures of several of these materials and conducted preliminary investigations of their luminescence spectra [16]. Because we propose to extend these investigations in the future, more details of these results are included in the renewal proposal.

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