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SPATIALLY ISOLATED REDOX ORBITALS - AN UPDATE

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ABSTRACT

The concept of the "spatially isolated orbital" was introduced to rationalize the unusual optical and magnetic properties determined for metal chelate complexes, ML_3^{n+}, in which a chelate ligand, L, as 2,2'-bipyridine possesses low energy π^* orbitals. Optical excitation or electrochemical reduction produces a species whose effective symmetry is that of the ligand alone. This review discusses the results associated with the redox orbital emphasizing anomalies that occur.

INTRODUCTION - "It is only when you are pursued that you become swift" - Kahlil Gibran

The "spatially isolated orbital" can be defined as a degenerate or near degenerate orbital existing in close spatial proximity to equivalent orbitals The effect upon the optical and electrochemical properties of d^6 metal chelates of general formula ML_3^{n+}, $ML_2L'^{n+}$, ML_2^{n+} is the focus of this paper. The manifestation of this phenomenon can be as direct as the observation of a dual emission from the lowest excited states[1,2] of a mixed ligand as $[Rh(bpy)_2phen]^{3+}$ where one emission lifetime and spectrum is characteristic of the "bpy" portion of the molecule and another emission characteristic of the "phen" portion of the molecule. More subtle occurrences have been observed as the observation of polarization (photoselection) values[3,4] (and related details) for the $[Ru(bpy)_3]^{2+}$ consistent only with the localization of the excited state one of the bpy ligands of the molecules. The concurrent observation of regular cyclic voltammetry patterns[5] for the $[Ir(bpy)_3]^{3+}$ and $[Ir(phen)_3]^{3+}$ suggests that the concept extends beyond these optical orbital examples. Indeed, the pattern of three closely spaced one electron reduction waves followed by three closely spaced one electron reduction waves found for

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the Ir(III) complexes has recently been duplicated for the $[Ru(bpy)_3]^{2+}$ complex using low temperature voltammetry techniques.[6] This latter result, subsequent to the observation of unusual ESR spectra[7] for the one, two and three electron reduction products of $[Ru(bpy)_3]^{2+}$, indicates the correlation of optical and redox orbital behavior (eqn. 1,2)

$$RuL_3^{2+} + h\nu \rightarrow {}^*[Ru^{(+3)}L^{-}L_2]^{2+} \qquad (1)$$

$$RuL_3^{2+} + e \rightarrow [Ru^{(+2)}L^{-}L_2]^{+} \qquad (2)$$

The occurrence of the spatially isolated orbital and the variety of manifestations in optical, magnetic and electrochemical measurments appears to require, at minimum, a ligand species, L, that possesses a low energy π antibonding orbital into which the optical or redox electron can be placed. Therefore, for both the species generated by the optical and the electrochemical processes, many of the properties of the resultant species are those of a type of metal containing heterocycle. This classification has been useful in rationalizing, for example, the similarity of the excited state resonance Raman[8] of $^*[Ru(bpy)_3]^{2+}$ and that obtained[9] by us for the one, two and three electron reduced complexes of $[Ru(bpy)_3]^{2+}$. But the fact that the optical process involves a "localized exciton" while the electrochemical process is concerned with "localized electrons" suggests that the correlation must be applied with caution since the quantum mechanics, kinetics and thermodynamic properties for the two types of system must differ in some details.

The fact that more than one electron can be added to the tris chelate system and the long lifetime (stability) of the reduced species are in contrast with the short lifetime of the optical species and the relative difficulty of exciting two electrons into ligand orbitals. The net result is that sufficient experimental data for the reduced species are available such that the detail of the spatially isolated redox orbitals can be better elaborated than that of the optical orbital. Moreover, various anomalies now become apparent that may require new directions to comprehend the redox orbital, therefore this manuscript will review some of the most recent results, some already published but much of it new data soon to be published. The ultimate result of such a probing will, at minimum, be a detailing and minor modification of the spatially isolated orbital concept. At maximum, a substantial restructuring of the model and even the development of a new model may be required to rationalize some of the most unusual results.

"The Speed of a Runaway Horse Counts for Nothing" - Jean Cocteau

RESULTS

The purposes of this research are

i) elaboration of the magnetic and electronic properties of these electrochemically generated materials by a variety of electrochemical and spectroscopic methods and

ii) construction of a model capable of rationalizing the "normal" and anomalous quantum mechanical, thermodynamic and kinetic properties of these systems.

The following section presents data organized according to the methodology employed.

a) Cyclic Voltammetry and Theoretical Results

Vital to the success of all the experiments, in particular voltammetry, has been the ability to produce ultradry and clean nonaqueous solvents, dimethylformamide (DMF) and acetonitrile (AN), capable of a near seven volt potential window. The dry solvent not only enables the identification of an unusual physical phenomenon but suggests a chemical dimension that could be exploited to produce distinctive results. For example, the ability to produce highly reduced stable species in quantity does produce a potent reducing agent that likely has multielectron reducing character.

Key results acquired at low temperature in AN and DMF were the voltammograms[6] for the parent $[Ru(bpy)_3]^{2+}$ (I) and the tris complexes RuL_3^{2+} (II and III respectively) of 5,5'-diethylcarboxy-2,2'-bipyridine (5,5'-CO_2etbpy) and the 4,4'-diethylcarboxy-2,2'-bipyridine (4,4'-CO_2etbpy). The three and three-pattern obtained (six one electron waves) for complexes I and II is the prediction of the simple spatially isolated orbital model and, while not conclusive, is encouraging. A remarkable ten electron pattern has been measured for compound III indicating the presence in solution of an anion having an 8^- charge.

The low temperature voltammetry for a series of tris complexes of general formula $[Ru(bpy)_{3-x}L_x]^{2+}$ (n = 0,1,2,3) where L is a bidentate π-electron complex shows at least six one electron waves for these complexes. The following are the main results of these efforts:

1) A MNDO calculation[10] for the free ligands bpy, 4,4'-CO_2etbpy and 5,5'-CO_2etbpy can be used to rationalize the relative order of the reduction waves for the free ligands and the corresponding tris complexes. In addition, the extra waves (ten total waves) observed for the 4,4'-CO_2etbpy complex result apparently from placement of electrons in a second low lying empty π^* orbital of the ligand in the complexes.

2) Theoretical considerations enable generation of a linear relationship between the lowest energy absorption (or the emission energy) and the oxidation-reduction wave potential difference of the starting material for the mixed ligand Ru(II)-bpy complexes.[11] These considerations suggest an identification of the energy factors contributing to the three and three pattern observed, i.e. the spacings within a triplet. In addition, an ion pairing effect[11] with the tetraethylammonium cation occurs for the reduction products having four, five and six electrons.

b) Electron Spin Resonance.

The ESR studies have utilized a variety of structural perturbations including mixed ligand complexes, multielectron (greater than three electrons) and tridentate chelate ligand complexes to extend the original ESR work.[7]

The following are the main results of the studies with tridentate ligand complexes:

1) The g factors and frozen spectra for one and two electron reduced $[Ru(terpy)_2]^{2+}$ and $[Fe(terpy)_2]^{2+}$ require only an $S = 1/2$ spin Hamiltonian, i.e. no evidence for an $S = 1$ state is observed for the two electron product.[12] Such behavior is consistent with single chelate ring localization of the reduced electrons.
2) Unlike the bidentate chelate complexes, no fluid solution spectra can be observed for any of the reduced terpyridine complexes, perhaps indicating a shorter electron spin lattice relaxation time. This is consistent with the slightly larger g shifts measured for these complexes and may indicate slightly larger metal d-orbital character for these complexes.

For a series of tris chelates of 4,4'-dimethyl-2,2'-bipyridine, (Me_2bpy), 5,6-dimethyl-1,10-phenanthroline (Me_2phen) with Fe(II) and Ru(II)[13] and bpy with Os(II),[14] the following are the main conclusions.

1) The solution g values and linewidths are consistent with the data for reduced $[Ru(bpy)_3]^{2+}$, i.e. all one, two and three electron reduced complexes give $S = 1/2$, $g \sim 2.00$ spectra consistent with the spatially isolated model.
2) The ESR for the solid (precipitate from CH_3CN) two electron reduced products, $[Ru(bpy)_3]^0$ and $[Ru(Me_2phen)_3]^0$, exhibit large g shifts and very broad lines (> 10^2 Gauss) indicating a large amount of metal d character in the redox orbital for these species. A rationale for this effect is that near degeneracy of empty d and π ligand orbitals in these two electron species results in a kind of

electronic isomerism. Such behavior parallels the photochemical properties of the parent system for which dd* and dπ* are sufficiently close in energy that dd* behavior can occur at room temperatures for both species. To clarify this behavior, the ESR of the $[Os(bpy)_3]^0$ was measured in the solid and is found to be identical to that in the frozen DMF (g ∿ 2.00, linewidth ∿ 80-90 Gauss thus a ligand localized radical). The parent $[Os(bpy)_3]^{2+}$ is known to have a much larger splitting between the lowest dπ* emitting state and the higher dd* photoactive state, therefore the absence of the large g shift and the broad line for Os(II) indicate that electronic isomerization is a reasonable rationale for the behavior of the solid reduced Ru(II) complexes.

3) The temperature dependence of the linewidths for the one, two and three electron species of these complexes is comparable to that reported by Motten,[7] i.e. the one electron product gives an activation energy, $E_{th} \approx 1000\ cm^{-1}$ approximately twice that for the two electron product. The three electron linewidth does not vary with temperature.

For the multielectron ($n \geq 4$ electrons) reduced products of $Ru[(5,5'\text{-}CO_2etbpy)_3]^{2+}$ (II), $[Ru(5,5'\text{-}\phi bpy)_3]^{2+}$ (IV) and $[Ru(bpz)_3]^{2+}$ (V) quite unusual results[15] have been acquired. Unfortunately, none of the reduction products of the $[Ru(4,4'\text{-}CO_2etbpy)_3]^{2+}$ complex are stable on the electrolysis time scale thus precluding ESR data for these species.

1) The four, five and six electron reduction products of both 5,5' species are all paramagnetic and each species exhibits an $S = 1/2$ spectrum indicating that the electrons do not couple magnetically, i.e suggesting the existence of spatially isolated orbitals as for the one, two and three electron species.

2) While the g factors and temperature dependent linewidths of the one, two and three electron reduction products for the complexes II and IV are nearly identical to those for the corresponding reduction products of the $[Ru(bpy)_3]^{2+}$ complex, the four electron product signal for II and IV disappear slightly above the freezing point while the linewidth of the five and six electron reduction products actually narrows as temperature increases.

3) The occurrence of three g tensor components in the frozen solution, when added to the fact that the six electron product is not diamagnetic as predicted by a simple three orbital model, makes it apparent that the orbitals of the fourth, fifth and sixth electrons must not be the same as those of electrons one, two and three. Such a result for these complexes has been predicted by the MNDO calculation[10] done for these systems.

4) As do the other complexes, $[Ru(bpz)_3]^{2+}$ (bpz = 2,2'-bipyrazine), exhibits a $g \approx 2$ and a temperature dependent linewidth broadening for the one electron product (but $E_{th} \approx 500$ cm^{-1}). The most unusual result is observed for the four electron product where the lineshape both in frozen and fluid solution suggests the presence of more than one paramagnetic moiety. That the two species are not paramagnetic decomposition products is evidenced by the fact that postelectrolysis voltammetry does not indicate decomposition, and that repetitive freeze and thaw cycles do not alter the ESR signal.

The ESR of mixed ligand complexes[16] of formula $[Ru(bpy)_2L]^{n+}$ where L = oxalate, n = 0 and L = ethylenediamine, n = 2+ was determined with two stable reduction products (electrolysis time scale) obtained for L = en in both CH_3CN and DMF solvents and two for L = en only in DMF. The following are the salient points for these systems.

1) Fluid and frozen solutions give $g \approx 2.00$ as for the other complexes and no evidence for $S > 1/2$ behavior is found for any reduced species.

2) Temperature dependent line broadening is observed for the one electron reduced complex having L = ox and both the one and two electron L = en complexes. E_{th} for the one electron complexes are $\sim$700 cm^{-1} while the two electron E_{th} is $\sim$400 cm^{-1}. Line broadening for the two electron reduction is not expected since the two electron reduction product for this bis bpy complex (one electron per bpy) would be expected to be analogous to the three electron product of the tris bpy complex.

The ESR data[17] for complexes of formula $[Ru(bpy)_{3-x}pq_x]^{2+}$, where x = 0,1 and pq = pyridylquinoline, do offer some interesting results. Cyclic voltammetry[11] indicates that the pq ligand is easier to reduce than the bpy. The following are the key points for these complexes.

1) The g factor and T dependence of the first three reduction products of $[Ru(pq)_3]^{2+}$ are similar to those of $[Ru(bpy)_3]^{2+}$.

2) For the $[Ru(bpy)_2pq]^+$ species, fluid solution spectra are, unlike those of other tris π chelates, asymmetric in the fluid range even up to room temperature.

3) Most noteworthy is the absence of any temperature dependent ESR linewidth for the $[Ru(bpy)_2pq]^{+,0}$ species (one and two electron reduction products).

4) The fluid solution ESR spectra of the $[Ru(bpy)_2pq]^-$ shows an asymmetric pattern that appears to result from the overlap of two closely spaced radical species (not fine structure).

To summarize, the voltammetry and ESR data for the Os(II) complexes, mixed ligand complexes of Ru(II), and multielectron species of Ru(II) do suggest the occurrence of unique magnetic and electronic interactions that can, in part, be rationalized by the spatially isolated orbital model. But some observations raise questions that indicate the need for, at minimum, some detailing or some modification of the electron hopping model. Such questions as,

1) Why are the six electron species paramagnetic ?
2) What is the origin of the temperature dependent line narrowing for the multielectron products?
3) Why are "dual radical" spectra measured for $[Ru(bpz)_3]^0$ and $[Ru(bpy)_2pq]^-$?
4) Why is temperature dependent broadening observed for the two electron reduction product of $[Ru(bpy)_2en]^0$? Can the insulating en ligand participate in a facilitated electron hopping with the π bpy ligands?

Answers to these questions can be derived from both additional ESR measurements and from other spectroscopic measurements.

c) Electronic Absorption Spectra of Reduced Complexes.

Our suggestion that the voltammetry pattern and ESR data imply existence of a bpy^- moiety stimulated us to attempt to identify a ligand based intervalence transition

$$[Ru(bpy)_2bpy^{-1}]^+ + h\nu \rightarrow [Ru(bpy^{-1})(bpy)_2]^+ \qquad (3)$$

for the reduced species as has been obtained for metal dimer complexes containing metals in two oxidation states (i.e. Ru^{II}-Ru^{III}). The Hush theory[18] for such mixed oxidation state species predicts that, for the localized valence state limit, $E_{opt} \approx 4E_{th}$. Our measurement of E_{th} from ESR of $\sim$1000 cm^{-1} thus enabled an estimation of the $E_{opt} \approx 4000$ cm^{-1}. The following results[17] have been obtained for the reduction products of $[Ru(bpy)_n(pq)_{3-n}]^{2+}$ (n = 0,1,2), $[Os(pq)_3]^{2+}$ and $[Ru(biq)_3]^{2+}$ where biq = 2,2'-biquinoline.

1) One, two and three electron reduction products exhibit UV and visible spectra analogous to $[Ru(bpy)_3]^{2+}$ (number of band and intensity).
2) The intensity of a band assigned as the intervalence transfer band in the 5000 cm^{-1} - 4000 cm^{-1} region for the different complexes is increased by a factor of 5-15 relative to that of the $[Ru(bpy)_3]^{2+}$. The origin of the intensity enhancement appears to be a through space π interaction between the larger π ligand rings of pq and biq.

3) The shift of the intervalence band to higher energy occurs for the mixed ligand complexes consistent with the Hush theory.

The following result has been obtained for the $[Ru(bpy)_2en]^{2+}$ reduction products.[16]

1) The one electron reduction product exhibits a broad band centered at 4000 cm^{-1} (the instrumental limit) with an ε of 250 but the spectrum of the two electron product does not indicate any absorption band at the instrument limit. The absence of the intervalence band for this two electron reduction product of the bis bpy complex is consistent with the absence of this band for the three electron reduction product. But such a result would not be consistent with the temperature dependent ESR line broadening occurring for the two electron product.

d) Nuclear Magnetic Resonance of the Reduced Complexes.

The absence of spin-spin coupling for the reduced systems having more than one unpaired electron and the absence of hyperfine splitting for any of the reduced Ru complexes has frustrated our efforts to obtain details of the wave function for these species that might enable verification of the electron hopping model. The lack of ESR hyperfine likely results from the kinetic process that broadens the ESR line (i.e. a short electron spin-lattice time (T_1)), thus suggesting that NMR spectra could be observed for these paramagnetic samples. Therefore, Dr. Yasuhiko Ohsawa did initiate proton Fourier transform NMR measurements on a Bruker WM 250 spectrometer. The following results[20] were obtained:

1) ^1H NMR paramagnetic shifts were measured for $[M(bpy)_3]^-$ and $[M(bpy)_3]^+$ (M = Fe(II), Ru(II) and Os(II)) in deuterated DMSO and deuterated CH_3CN and by comparison with free bpy and the reduced $[Ru(4,4'\text{-}(Me_2bpy)_3]^{2+}$ the spectral lines were assigned.
2) The small ESR g factor anisotropy, the linear correlation of the shifts with the square of the linewidth[21] and the reversal of the sign[21] for the contact shift upon substitution of the CH_3 at the 4 and 4' positions imply the absence of dipolar contributions to the measured shift suggesting that the radicals can be treated as π electron radicals. Therefore the simple McConnell relation[22] can be used to calculate the spin density at the various positions. The relative spin densities calculated for the $[Ru(bpy)_3]^-$ species correlate well with those derived from the MNDO calculation done for the ligand bpy, however the limited spin density data available from the $[Ru(bpy)_3]^+$ and the bpy^- species indicate that the absolute magnitude of the spin densities for the three electron species

are smaller than expected suggesting a complication in the magnetic susceptibility.

3) Examination of the NMR linewidth for $[M(bpy)_3]^+$ complexes as a function of temperature permits an estimate of the intramolecular ring hopping. The magnitude of E_{th} is identical to that obtained from ESR.

e) Resonance Raman Spectra for Reduced Species.

A desire to produce additional evidence for the localization of the charge and to define the vibronic coupling associated with the localization resulted in the initiation of resonance Raman studies for the reduced species. The main results of this effort are as follow:

1) The Raman spectra of $[Ru(bpy)_3]^{2-n}$ were investigated. The spectra of the n = 0 and n = 3 ions are those of bpy and bpy^- as would be predicted from any of the models. The spectra of the n = 1 and n = 2, however consists of a composite of bpy and bpy^- spectra indicating the presence of both moieties in the complexes and thus arguing strongly for localization. The spectrum of the n = 1 ion is very similar to that observed for the excited state and thus it would appear tha the REDOX and optical orbitals are similar.

2) Results for the multielectron reduced products[16] (number of reduction electrons greater than three) suggest that localization is occurring for the fourth, fifth and sixth electron of the $[Ru(5,5'\text{-}CO_2etbpy)_3]^{2+}$ complex but the redox orbital for the fourth, fifth and sixth electron is distinct from that of the first, second and third electrons.

DISCUSSION

To order the data available, this discussion will divide the materials according to gross structural features into three groups:

a) parent tris, $[ML_3]^{n+}$, with one, two and three reduction electrons,

b) multielectron species, $[ML_3]^{n+}$, number of reduction electron equal to 4, 5, and 6, and

c) mixed ligand complexes, $[ML_2L']^{n+}$

The discussion will emphasize the anomalies and where possible suggest experiment to clarify the situation.

a) The Parent Tris Complexes. A continuation of the work for one, two and three electron reduction products of tris compounds will require, primarily, some extension of the methods currently used rather than extension of the materials. For example, the major portion of the ESR spectroscopic studies have been done in the range from 77K to room temperature using X-band methods. At 77K in glassy solutions, some asymmetry in the single line ESR signal is apparent for many complexes. Therefore the behavior of the one, two and three electron products at temperatures approaching liquid helium temperatures must be determined to answer these questions.

> Is the signal observed still essentially an $S = 1/2$ signal for all three samples? What is the asymmetry origin?

Here, examination of the $[Os(bpy)_3]^{2+}$ reduction products and comparison with $[Ru(bpy)_3]^{2+}$ reduction products could be valuable since the 77K spectra of the $[Os(bpy)_3]^{+,0}$ species indicate that some portion of the asymmetry does result from the presence of the larger Os(II) species. Whether such a difference is the result of a kind of external heavy atom effect or the result of a finite spin density at the metal atom could be answered if accurate hyperfine data could be obtained for all atoms in the ligand ring system other than the metal. This may now be possible using the NMR methods recently employed to acquire proton contact shifts for the reduced $[Ru(bpy)_3]^n$ complexes. The direct acquisition of C^{13} spin densities for the bridging carbon atoms of the ligand would mean that only the nitrogen and metal atom spin density would be absent for the reduced complex. The MNDO calculation[8] for the free ligand system does produce excellent correlation of the experimental spin density with the theoretical, however the major fraction of the spin density is predicted to be on the bridging carbon atoms and the nitrogen atoms.

To verify the weak coupling of the spins for the unpaired electrons, ESR spectra at higher field must be obtained. Earlier attempts at K band were not successful since the dielectric loss occurring for DMF or CH_3CN solvents will not permit the coupling of the microwave power to the ESR cavity even at 77K. Now some voltammetry results in lower dielectric constant solvents as methylene chloride and dichloroethane indicate that such an approach may permit determination of K-band spectra, at least for the first two reduced species.

As noted, the temperature dependent ESR linewidth data result in an activation energy of approximately 1000 cm^{-1} for a number of tris complexes while the optical energies of the so-called intervalence transfer process (eqn 3) range in energy from 4000 cm^{-1} to 5000 cm^{-1}. This is consistent with that predicted in theories[18,23] of electron transfer for the limit of a localized state. Moreover, the absence of line broadening for the three electron species of any tris complexes correlates with the disappearance of the so-called intervalence transfer bands. The following, however, cannot be rationalized within the model as presently constructed.

1) The activation energy for two electron tris products derived from ESR data is one half of the one electron activation energy whereas E_{opt} is about the same.
2) The resonance Raman spectra for the one and two electron products exhibit only totally symmetric vibrational modes in the high frequency ligand region, no antisymmetric modes have been determined to date. However, the PKS model[23] for mixed valence complexes suggests the existence of, at least, one antisymmetric mode responsible for the localization.
3) The one electron product for the $[Ru(biq)_3]^{2+}$ complex exhibits the usual intervalence transfer band (with much higher intensity), however the two electron product does not give a band in this region. The experimental conditions and the intensity of the band make it unlikely that this band could be overlooked for this species.
4) The one electron reduction product[15] for the $[Ru(bpz)_3]^{2+}$ does give a normal ESR spectrum, an $S = 1/2$ spectrum with $g \approx 2.00$, however the fluid and frozen solution spectra for the two electron reduction product is unusual with a double peak occurring in the $g \approx 2.00$ region and no other structure observed (nothing in the low field $\Delta M_S = 2$ region).

To clarify the first point NMR linewidth measurements can be used to verify the kinetics parameters obtained from ESR measurements. The measurement of NMR contact shifts for the one electron and three electron species not only produced paramagnetic contact shifts and spin densities but the temperature dependent NMR line broadening gives an activation energy equal to that measured from the ESR line broadening. Acquisition of temperature dependent NMR linewidth data for the two electron species both in deuterated DMF and in deuterated dichloroethane, will allow comparison of the linewidth data from NMR and ESR, thus permitting exploration of various rationale for the two to one ratio of the activation energy for the +1 and 0 complexes. If the kinetic process occurring truly is an intramolecular electron transfer process rather than some line broadening process specific to the ESR experiment, then the temperature dependent NMR line broadening should produce activation energies comparable to those from ESR.

Similarly, the search in our Raman studies has been for a ring expansion mode or some similar ligand localized mode with a frequency of 1000 cm^{-1} or greater (point 2). The possibility that the asymmetric mode involved in the localization is a low frequency metal mode is now being investigated. The examination of the polarization ratios will be critical since theory[24] predicts that the occurrence of vibrational modes coupled to degenerate excited states would give Raman lines with depolarization ratios of 1/8. To date all of the high frequency modes[25] observed have ratios of 1/3, that predicted for resonance with nondegenerate states indicating that the electronic state is behaving as an orbitally nondegenerate state.

The examination of the ESR and electronic absorption spectra for the $[Ru(biq)_3]^{2+}$ and $[Ru(i\text{-}biq)_3]^{2+}$ reduction products (i-biq is 2,2'-i-biquinoline) may be useful in evaluating the degree of coupling of the electrons for the two and three electron products as well as understanding the third anomaly. The parent complex, $[Ru(i\text{-}biq)_3]^{2+}$, is known to have a ligand localized $\pi\pi^*$ emitting state.[26] If such results for the parent species can be extrapolated to that situation for the reduction products (as it has with some degree of success for the other systems), then the ligand localized redox electrons for these reduced species may interact with one another even less than the ligand localized optical electrons. The magnitude of the g anisotropy at low temperatures could be a measure of the relative amount of the d orbital character.

An explanation of the absence of the intervalence absorption process for $[Ru(biq)_3]^0$ may be aided by examination of the temperature dependent ESR linewidth. If an S = 1/2 spectrum is observed and line broadening does not occur, the strong localization could occur such that the intervalence band shifts to higher energy and is hidden by other bands. Alternatively, the spatial extent of the ligands may be such that coupling can now occur between the two electrons resulting in a true S = 1 system. This should be readily apparent by examination of the ESR at 77K.

Examination of the resonance Raman, in particular for the reduction products of $[Ru(biq)_3]^{2+}$, could be invaluable in clarification of the results for this two electron product. If the electrons do couple for the $[Ru(biq)_3]^0$, i.e., the system is delocalized then the type of spectral pattern observed for the one, two and three electron reduction products of $[Ru(bpy)_3]^{2+}$ where the Raman spectra could be understood as containing both a bpy and bpy^{-1} species likely would not be repeated. In particular, the two electron spectra would not be a combination of the spectra of the parent and three electron species but would exhibit a third type of biq ligand mode pattern.

The fourth point, the ESR result for the two electron reduction product, $[Ru(bpz)_3]^0$, is quite unusual. The K-band ESR spectra would be invaluable in distinguishing between a fluid media spin-spin interaction (no legitimate example has been found) and the overlapped spectra of two species, perhaps geometric or electronic isomers. The low dielectric constant solvent, dichloroethane, does have a reduction window adequate for this purpose. Concurrent electronic absorption and resonance Raman spectra for the reduction products of $[Ru(bpz)_3]^{2+}$ may help to clarify the ESR result for the two electron product.

b) Mixed Ligand Complexes $[ML_2L']^{n+}$. The spectroscopic data acquired for mixed ligand complexes also demonstrate inadequacies in the model.[18,23] Since these have been verified by repeated experiment and by structural variation, the origin of these anomalies could be that the model intended for dimer and trimer metal containing systems must be altered specifically for these metal heterocycles.

For example, the ESR signal for the two electron reduction product, $[Ru(bpy^-)_2en]^0$, does broaden with temperature and give an activation energy approximately one half of the one electron product rather than a temperature independent linewidth as would be predicted if electrons cannot be transferred to the insulating en ligand. The absorption spectrum of the one electron species produces a weak intervalence absorption band at the limit of the Cary 14 spectrometer ($\sim$4000 cm^{-1}) that is not apparent for the two electron product. The verification of these results by examination of the ESR and electronic spectra for comparable chemical species as well as by extending the spectral region examined will be attempted. Examination of the one and two electron reduction products of $[Ru(bpy)_2(CN)_2]^0$ should be possible since these two species are known to be stable on a long time scale. Subsequent to the ESR and electronic spectra for these reduced species, resonance Raman spectra for the one and two electron species, should give the vibrational patterns associated with a bpy and bpy^{-1} mode.

The ESR and electronic spectra and the temperature dependent linewidth data for the reduction products of the mixed ligand $[Ru(bpy)_2pq]^{2+}$ afford some useful insight into the barrier changes caused by a large perturbation (i.e. pq energy levels different from bpy). The g factors are $\not\approx$ 2.0 for the $[Ru(bpy)_2pq]^{+,0}$ species and are thus comparable to those observed for all other species. However, unlike the other tris π diimine complexes, the linewidth for these one and two electron species do not vary with temperature. The electronic absorption spectrum for the $[Ru(bpy)_2pq]^+$ exhibits an intervalence absorption band at 4500 cm^{-1} that is more intense than the corresponding band in $[Ru(bpy)_3]^+$. The intervalence absorption band for the two electron reduction product occurs at the same energy as the one electron product but has an intensity only one half of the one electron species. The absence of ESR line broadening can be interpreted to mean that the barrier for the thermal process is very large for an asymmetric barrier. However the fact that the ligand based intervalence transfer energy for these two reduced species is comparable to that of other reduced tris complex systems for which an ESR thermal broadening is measured cannot at present be rationalized In addition, the ESR spectrum of the three electron reduction product is complex with a double peak solution spectrum that does not appear to be due to an S = 1 system or g factor anisotropy. The use of K-band ESR may be enlightening here as well.

For each of the reduced mixed ligand systems the NMR method could, if feasible, be invaluable in providing spin density information as well as kinetic information to corroborate the ESR kinetics. Thus, with the $[Ru(bpy)_2pq^-]^+$ and $[Ru(bpy)(bpy^-)(pq^-)]^0$ species, the presence of spin density on the bpy and pq could be quantitated by comparison with the NMR of the analogous reduced parent compounds, $[Ru(bpy)_3]^{2+}$ and $[Ru(pq)_3]^{2+}$. For those systems as for the $[Ru(bpy)_2pq]^-$ where an anomalous double peaked ESR spectrum is observed, the NMR may, with the K-band ESR, enable identification of the double peaks as separate bpy^{-1} and pq^{-1} radical species in this ion.

3. <u>Multielectron Complexes</u> (four, five and six reduction electron complexes). Electrogeneration of solutions of stable reduced complexes containing one through six electrons is unique. Moreover, some remarkable magnetic and electronic properties have been observed for these materials. At this time only two such materials, $[Ru(5,5'\text{-}CO_2etbpy)_3]^{2+}$ and $[Ru(5,5'\text{-}\phi_2bpy)_3]^{2+}$ produce six stable species. Others, as the $[Ru(bpz)_3]^{2+}$, $[Ru(pq)_3]^{2+}$, $[Ru(biq)_3]^{2+}$ and $[Ru(4,4'\text{-}CO_2etbpy)_3]^{2+}$, do give voltammograms at room temperature that produce more than three and as many as ten one electron reduction waves in the potential window of the DMF or CH_3CN. However, the best methods developed indicate that even in the dry, oxygen free solvents, chemical factors lead to decomposition after a short time (∿10-30 minutes), in particular for the multielectron species.

The results presented suggest that clarification of the paramagnetism of the six electron products and the absence of the T dependent line broadening will be our primary task for these materials. Consequently, K band ESR spectra and low temperature ($T < 77K$) X-band ESR spectra will be measured for these systems. The K-band spectra may enable spin-spin interaction to be found for these weakly coupled electron systems while the temperature dependent spectra for these systems may determine the presence of low lying spin states. The results do indicate that the g anisotropy is larger for four, five and six electron species than for one, two and three.

Absorption spectra have been measured for the reduction products of $[Ru(5,5'\text{-}(CO_2et)_2bpy)]^{2+}$ and an intervalence charge transfer band cannot be observed, perhaps because intense low energy ($\pi^*\text{-}\pi^*$) bands associated with the reduced ligand overlap the lowest energy absorption region. Here, the use of low temperature absorption methods should allow resolution of weak bands occurring in the tail of the intense band. Resonance Raman studies of these multielectron species should be invaluable in determining if these data are consistent with the single chelate ring orbital model for the one to three electron species and to verify that the orbital associated with the four to six electron species be correlated with a second low lying energy orbital of the free ligand rather than the first empty orbital (LUMO) as for the one to three electron species.

To acquire a more quantitative description of the situation for the four to six electron species, NMR spectra will be acquired to obtain spin density data that can be correlated with the MNDO wave function available for these species.

Key questions that must be answered for these multielectron species are:

1) Are the electrons for the four-six electrons species "localized" in a single chelate ring ?
2) Why does temperature dependent ESR line broadening not occur?
3) What is the origin of the larger g anisotropy for these systems?
4) Does spin pairing occur for the four and five electron species?
5) Why is not a spin coupled (S=1) state observed for the six electron species? (Even if fourth, fifth and sixth electron species are each localized on a single ligand, thus not coupled, some coupling with the first electron on a ligand should be observed to produce a "vertical" triplet species between the two electrons localized on a single ligand.)

SUMMARY

To suggest that a "Conclusion" can now be presented is both premature and pessimistic. Quite apparently this localization phenomenon is not yet adequately characterized experimentally and, until it is, a totally appropriate model will not be possible. In the interim, the Hush[18] and PKS[23] model do provide a quite adequate framework to understand many of the gross features of the results. At this point, the principal features of the unusual electronic and magnetic properties of these reduced species are:

1) The propeller shaped tris diimine complexes have a unique ability to store charge (as many as six electrons) primarily in the ligand π-electron system.
2) The magnetic properties of the multielectron heterocycles indicate an absence of spin-spin coupling for multi-electron reduction products such that species with one through six electrons appear as effective one electron systems.
3) ESR, vibrational, and electronic spectroscopy, suggest the presence of potential barriers between the chelate rings resulting in a localization of the reduction electrons upon the individual chelate rings.

4) Temperature dependent magnetic resonance data permits description of a kinetics process, likely "intramolecular electron hopping", associated with the reduced species.

Ultimately, the participation, if any, of the solvent and counter ions in stabilizing the reduced species and localizing the charge must be examined. The convenience of the coordinating DMF and CH_3CN solvents can indeed disguise the function of the solvent in these reduced systems. While the combination of ESR, electronic spectra, resonance Raman, NMR and cyclic voltammetry measurements for a wide range of chelate systems certainly cannot be rationalized by localization of the reduction electron totally on the solvent, a type of solute-solvent complex might be possible. The occurrence of a paramagnetic six electron species and the recognition that solvent can play a role in the optical spatially isolated model[28] necessitates that such solute-solvent species be considered.

"It is better to destroy one's own errors than those of others" - Democritus

REFERENCES

1. W. Halper and M.K. DeArmond, J. Lumin. 5 (1972) 225.
2. M.K. DeArmond and C.M. Carlin, Coord. Chem. 36 (1981) 325.
3. C.M. Carlin and M.K. DeArmond, Chem. Phys. Lett. 89 (1982) 297.
4. I. Fujita and H. Kobayashi, Inorg. Chem. 12 (1973) 2758.
5. J.L. Kahl, K.W. Hanck and M.K. DeArmond, J. Phys. Chem. 83 (1979) 2611.
6. Y. Ohsawa, M.K. DeArmond, K.W. Hanck, D.E. Morris, D.G. Whitten and P.E. Neveux, Jr., J. Am. Chem. Soc. 105 (1983) 6522.
7. A. Motten, K.W. Hanck and M.K. DeArmond, Chem. Phys. Lett. 79 (1981) 541.
8. R.F. Dallinger and W.H. Woodruff, J. Am. Chem. Soc. 101 (1979) 4391.
9. R.J. Donohoe, S.M. Angel, K.W. Hanck, D.W. Wertz and M.K. DeArmond, J. Am. Chem. Soc. 106 (1984) 3688.
10. Y. Ohsawa, M. Whangbo, M.K. DeArmond and K.W. Hanck, Inorg. Chem. 23 (1984) 3426.
11. Y. Ohsawa, K.W. Hanck and M.K. DeArmond, J. Electroanal. Chem. 175 (1984) 229.
12. D. Morris, K.W. Hanck and M.K. DeArmond, J. Electroanal. Chem. 147 (1983) 115.
13. D. Morris, K.W. Hanck and M.K. DeArmond, J. Am. Chem. Soc. 105 (1983) 3032.
14. D. Morris, K.W. Hanck and M.K. DeArmond, Inorg. Chem. in press (1985).

15. D. Morris, T. Vess, R.J. Donohoe, K.W. Hanck, D.W. Wertz and M.K. DeArmond, J. Am. Chem. Soc., submitted (1985).

16. D. Morris, D. Tait, K.W. Hanck and M.K. DeArmond, Chem. Phys. Lett., submitted (1985).

17. D.B. MacQueen, D. Morris, K.W. Hanck, D.W. Wertz and M.K. DeArmond, J. Am. Chem. Soc., submitted (1985).

18. N.S. Hush, Chem. Phys. 10 (1975) 361.

19. G.A. Heath, L.J. Yellowleas and P.J. Braterman, Chem. Phys. Lett. 92 (1982) 646.

20. Y. Ohsawa, C.G. Moreland, K.W. Hanck and M.K. DeArmond, J. Am. Chem. Soc., submitted (1984).

21. W. D. Horrocks, in NMR of Paramagnetic Molecules, G.N. LaMay, W.DeW. Horrocks, Jr., R.H. Holm, Eds., Academic Press, New York (1973).

22. H.M. McConnell and D.B. Chesnut, J. Chem. Phys. 28 (1958) 107.

23. S.B. Piepho, E.R. Krausz and P.N. Schatz, J. Am. Chem. Soc. 100 (1978) 2006.

24. R.J. Clark and B. Stewart, Structure and Bonding 36 (1979) 1.

25. R.J. Donohoe, S.M. Angel, D.W. Wertz and M.K. DeArmond, unpublished results.

26. P. Belser, A. von Zelewsky, A. Juris, F. Barigelletti, A. Tucci and V. Balzani, Chem. Phys. Lett. 89 (1982) 101.