the theory would be adequate for one problem and not the other, and perhaps additional ingredients exist in the self-exchange kinetics that lead to a fortuitous agreement or perhaps a simple relationship between optical and thermal electron transfer does not exist for ammine complexes. (2) One criterion that has been cited in support of a delocalized description for the dimer $[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{5+}$ is the absence of a significant solvent dependence.[1] However, given the relatively slight dependence of E_{op} on solvent in the 4,4′-bpy dimer, noting that in the related, valence-trapped system $[(bpy)_2ClRu(L)RuCl(bpy)_2]^{3+}$ the substitution of L = 4,4′-bpy by L = pyrazine decreases $\delta E_{op}/\delta(1/D_{op} - 1/D_s)$ by twofold, the solvent dependence criterion for delocalization may not be fully valid. (3) From the results obtained in an earlier experiment in which the solvent dependence of the metal-to-ligand charge-transfer band energy in $[(NH_3)_5Ru^{II}(py)]^{2+}$ was observed, it was concluded that solvent effects were dominated by the way in which specific solvent–ammine H-bonding interactions influenced the energy separation (ΔE) between the excited and ground states.[17] In that experiment E_{op} could be correlated with an empirical solvent basicity parameter, the so-called donor number, which is derived from the heat of solvation of $SbCl_5$.[18] In the decaammine dimer where ΔE = O (except for the small contribution from multiple IT transitions (Δ)), the specific solvent effect must appear in the solvent trapping term χ_s.[19] We find that multiple parameter fits of the type ($E_{op} - f$(donor number)) vs. $(1/D_{op} - 1/D_s)$ do give slightly improved correlations. In a more appropriately designed theory, specific solvent molecule–metal complex interactions may need to be included explicitly.[20]

Finally, although χ_s for D_2O falls within 3σ of the best-fit line, the positive deviation is probably significant since it appears to be a general phenomenon for mixed-valence complexes in water, independent of the ligand coordination environment.[21] We have speculated elsewhere[21] that one possible origin is in a contribution to solvent trapping from relatively high frequency solvent librations that have been observed in the Raman spectrum of water.[22]

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Temperature Dependence of the Doublet Lifetime in Chromium(III) Compounds

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The role of the lowest excited doublet state in chromium(III) photochemistry has been investigated diligently for the past quarter of a century.[1,2] Among numerous reviews, that by Kemp[3] is particularly pertinent to the issues we address here. The lowest doublet, unlike excited quartet states, frequently emits detectable phosphorescence even in room-temperature aqueous solutions, which facilitates the measurement of photophysical properties and encourages experimental investigations. With the introduction of lasers and improvements in electronic detection, it is now possible to characterize a wide variety of different Cr(III) compounds including, in particular, those with short lifetimes and very low luminescence yields.

Ligand substitution reactions may occur directly from the doublet state in some, many, or all compounds, but such reactions occur in competition with other decay mechanisms. The very basic question that we address here is, Which decay process is "lifetime-controlling" under what circumstances?

Assuming conditions such that there are no diffusive bimolecular quenching processes, it is common to distinguish four decay processes: nonradiative relaxation to the ground state k_{nr}; phosphorescence k_{rad}; chemical reaction k_{rxn}; and reverse intersystem crossing RISC to an excited quartet k_{risc}. Within this model, the doublet lifetime would be expressed as

$$1/\tau_{phos} = k_{rxn} + k_{risc} + k_{nr} + k_{rad}$$

The radiative rate is extremely small and nearly temperature independent.[4] The nonradiative rate usually refers only to a weak-coupling process that can be characterized at low temperatures. It also is fairly small, and its temperature dependence is insufficient to account for the large overall decay rates at room temperature.[3] The remaining two terms are expected to be more strongly temperature dependent. Either one or the other may be invoked to explain the fact that in room-temperature solutions the doublet lifetime is usually much shorter and displays more variation with temperature than it does under cryogenic conditions. A minor detail is that RISC need not be fully irreversible; there could be some probability of return to the doublet. That does not change the logic of the model; it simply requires multiplying k_{risc} by a branching ratio.

The above scheme is logically incomplete. One should entertain the possibility of additional nonradiative pathways that dissipate electronic energy as heat but do not lead to net chemical reaction. These might involve substantial nuclear motions and be inhibited in glassy or crystalline matrices at low temperatures but assume dominance in fluid solution at ambient temperatures. Since the pioneering work of Targos and Forster[5] showing that the temperature dependence of nonradiative decay can be quite complicated, even at low temperatures, there have appeared several additional studies on the same subject, which have received critical review.[3] The relevance to room-temperature processes remains obscure. The common practice[6-11] has been to persist with the four mechanism model summarized above and argue that "if it is not reverse intersystem crossing, then it must be chemical reaction that dominates." Forster[7] certainly recognizes that the short phrase "chemical reaction" needs further elaboration; presumably others do as well. He considers the possible role of geminate recombination following a "primary" dissociative reactive step. Endicott and co-workers[12] propose a mechanism that they consider to be distinct from both nonradiative decay and chemical reaction, but which, in a way, accommodates both. They suggest a curve crossing that populates a "reactive ground-state intermediate" from which a branching is possible to form either photoproducts or the original ground state. They have in mind an associative intermediate or transition state.

Previous studies have attempted to identify processes occurring from the doublet by using a variety[3] of different kinds of mea-

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surements: quenching studies,[13] energy transfer,[1] solvent effects,[9-11] solid-state lifetimes,[14] and isotope effects.[9,14]

More direct are attempts to correlate doublet lifetimes with some estimate of barriers to RISC or chemical reaction.

The energy barrier to RISC should be proportional to the energy gap between the doublet and the excited quartet.

In most Cr(III) molecules the energy of the doublet state is known quite well, since absorption and phosphorescence emission are usually both observable at the same spectral position. Unfortunately, the energy of the lowest excited quartet is not as well known. In the absence of detectable fluorescence emission, the origin of the 0–0 transition to the excited quartet cannot be estimated by the generally accepted procedure of locating the "crossover" of the absorption and emission bands. Consequently, the doublet–quartet gap cannot be determined with certainty. However, the location of the quartet—and, therefore, the doublet–quartet energy gap—may be estimated from absorption spectra utilizing the 5% rule in the model developed by Fleischauer, Adamson, and Sartori.[15] This value we designate as E_{FAS}.

The FAS model was developed as an extrapolation from conditions of strictly octahedral symmetry (six identical ligands) and a low-temperature, glassy matrix. For room-temperature aqueous solution, the model is not as well validated. We will try the model as the best available and test later for internal consistency in our results.

In order to test the relation between lifetimes and energy barriers, two strategies are possible. The thermal energy may be kept constant by working at a single temperature as the energy barrier is changed systematically through chemical modification, or the barrier may be left constant as the available thermal energy is changed by varying the temperature.

The first approach was applied to a series of some 20 compounds in aqueous solution to demonstrate a correlation between the doublet lifetime and estimated energy barriers for RISC.[16] The lifetimes were below a microsecond, and the compounds were selected to have small doublet–quartet energy gaps (0–40 kJ mol^{-1}). There seemed to be an upper limit to possible values for the activation energy. Values greater than about 40 kJ mol^{-1} did not occur, but few measurements were made in that regime. The conclusion was that RISC dominated until the energy barrier to that process became too large. Probably, one should not expect RISC to dominate when the energy barrier is larger than 40 kJ mol.$^{-1}$ At room temperature, the Boltzmann factor would then be 3×10^{-8} or less. At that point, some other mechanism is almost bound to dominate.

The second approach, measuring the temperature dependence of the lifetime in order to extract an activation energy, has been used in several recent detailed studies of phosphorescence lifetimes in aqueous solution, as well as in various organic solvents.[9-11] In those cases, lifetimes were almost always much longer than a microsecond in duration. Activation energies tended to cluster around 40 kJ mol^{-1}, similar to the limit found in the work discussed above. The constancy of that energy gap led to the conclusion that RISC could not be important, since the barrier should not remain constant for a wide variety of compounds. To further support the hypothesis that there was a single mechanism common to all those many molecules, an analysis in terms of a Barclay–Butler plot was presented.[10,11] That analysis confirmed that a single mechanism applied in all compounds studied. Chemical reaction was inferred to be that dominant mechanism, although the exact limits of the meaning of that term were not specified.

Among recent work directly exploring the issue, therefore, one study defended the importance of RISC, which would be in accord with the preponderance of early thought,[17] as has been explained in reviews.[3] Several studies have argued against RISC. The question arises, now, whether the difference between the conclusions of the different studies is related to their use of different experimental approaches or to genuinely different mechanisms in different cases.

Table I. Phosphorescence Lifetimes,[a] Thermal Activation Energies,[b] and Spectral Energy Gaps for Cr(III) Compounds

molecule	τ_{phos},[c] ns	E_{meas}, kJ/mol	E_{FAS}, kJ/mol
$[\mathrm{Cr(urea)_6}]^{3+}$	0.7	0.0	0.7
$[\mathrm{Cr(ox)_3}]^{3-}$	1.2	5.4	16.4
$[\mathrm{Cr(NCS)_6}]^{3-}$	1.7	33.5	32.9
trans-$[\mathrm{Cr(NH_3)_2(NCS)_4}]^{-}$	5.5	26.9 (41.8)[d]	36.4 (31.4)[f]
trans-$[\mathrm{Cr(en)_2(NCS)_2}]^{+}$	8900	29.3 (31.8)[d] (25.5)[e]	53.8 (28.58)[f]
$[\mathrm{Cr(en)_3}]^{3+}$	1200	40.8 (41.8)[d] (43.9)[e]	58.0
trans-$[\mathrm{Cr(py)_4F_2}]^{+}$	98	49.9	61.5

[a] ±5%. [b] ±2 kJ/mol. [c] At 22 °C. [d] From ref 9. [e] From ref 17. [f] From ref 22.

We report here the measurement of the temperature dependence of the doublet lifetime in aqueous solution for a series of Cr(III) compounds with E_{FAS} ranging from 0 to 60 kJ mol^{-1} in order to determine the activation energy of the process that limits the lifetime of the doublet. We particularly consider short-lived species that could not be treated in previous studies. We incorporate the results of those measurements into the Barclay–Butler analysis. We conclude that RISC is the lifetime-limiting process in compounds with a small energy separation, that is, less than 30 or 35 kJ mol^{-1}. As the energy separation becomes larger, another process, which could be termed chemical reaction if that term is used loosely enough, becomes the lifetime-limiting mechanism. We do not address the issue of distinguishing chemical reaction from specific nonradiative mechanisms or the Endicott hypothesis.

Experimental Section

Chemicals. $[\mathrm{Cr(urea)_6}]^{3+}$ was synthesized according to the literature.[18] $[\mathrm{Cr(ox)_3}]^{3-}$ and *trans*-$[\mathrm{Cr(py)_4F_2}]^{+}$ were gifts from Dr. M. Cimolino. $[\mathrm{Cr(NCS)_6}]^{3-}$, *trans*-$[\mathrm{Cr(NH_3)_2(NCS)_4}]^{-}$, and $[\mathrm{Cr(en)_3}]^{3+}$ were obtained from Alfa Products. *trans*-$[\mathrm{Cr(en)_2(NCS)_2}]^{+}$ was synthesized according to the literature.[19] $[\mathrm{Cr(NCS)_6}]^{3-}$ was twice recrystallized from methanol. All other compounds were twice recrystallized from water. Recrystallizations were done under faint red light and the compounds stored in the dark until use. Solutions were made with deionized water; the concentration was adjusted so that the absorbance at the excitation wavelength was close to 0.6. All solutions were pumped continuously through a flow cell in order to avoid photolysis problems. The temperature was regulated by thermostating both the cell holder and the solution reservoir.

Techniques. Excitation was obtained in the lowest LF absorption band by using a mode-locked Spectra Physics argon ion laser. The excitation wavelength was usually 514.5 nm. In some runs the 458-nm argon line was used to shift the solvent Raman signals in order to confirm the identification of the chromium luminescence or to match more closely the LF absorption. The pulse width from the argon laser was less than 200 ps. In a few other instances luminescence was excited by using a synchronously pumped DCM dye laser operating in the red-orange. The pulse width for the dye laser was less than 10 ps.

The procedure used for the collection of data and for the kinetic analysis is described in a previous paper.[20]

Results

Phosphorescence decay curves were obtained for each molecule at four or five temperatures between 5 and 40 °C. Each decay curve could be fit by a single exponential, except that some species

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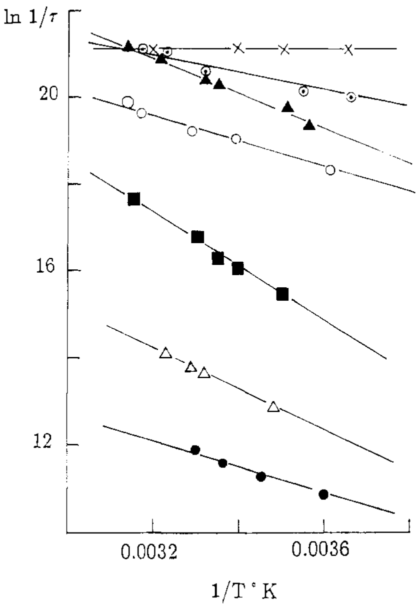

Figure 1. Arrhenius plots of the log of the total doublet decay rate vs. reciprocal temperature: (×) $[Cr(urea)_6]^{3+}$; (⊙) $[Cr(ox)_3]^{3-}$; (▲) $[Cr(NCS)_6]^{3-}$; (○) *trans*-$[Cr(NH_3)_2(NCS)_4]^-$; (●) *trans*-$[Cr(en)_2(NCS)_2]^+$; (△) $[Cr(en)_3]^{3+}$; (■) *trans*-$[Cr(py)_4F_2]^+$.

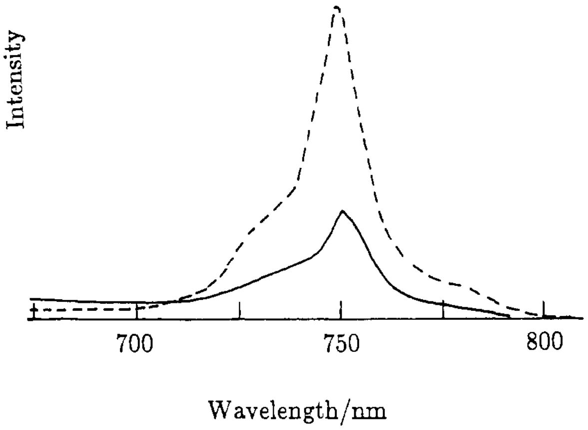

Figure 2. Temperature dependence of the emission spectra of *trans*-$[Cr(NH_3)_2(NCS)_4]^-$: solid line, 32 °C; broken line, 9 °C.

showed an additional small, very rapidly decaying component, which is discussed again below.

For each molecule, an Arrhenius plot of the log of the phosphorescence decay rate vs. reciprocal temperature was generated in order to determine an activation energy, E_{meas}. The Arrhenius plots are shown in Figure 1. The data for each molecule are adequately accounted for by assuming that a single process dominates over the temperature range investigated. The activation energies derived from the plots are shown in Table I.

Two of the long-lived molecules have been studied previously[9,17] under similar conditions. The results, shown in Table I, were close to ours.

Absorption spectra, recorded at various concentrations or with different cell lengths as needed to cover the required range of absorbances, were analyzed to determine E_{FAS}. The results are shown in Table I.

Emission spectra were also recorded for each molecule at each temperature. As an example, the total emission spectrum of *trans*-$[Cr(NH_3)_2(NCS)_4]^-$ at two temperatures is shown in Figure 2. Note the increase in the intensity contained in the "wing" to the high-energy side of the phosphorescent maximum as the temperature is increased. This behavior was also observed in the temperature-dependent emission spectra of $[Cr(NCS)_6]^{3-}$. We previously identified a very short-lived, weak, and broad emission in those two moleules with a prompt fluorescence (possibly from a state that is not completely relaxed thermally).[21] By considering spectra as well as decay kinetics at particular wavelengths in the wings of the emission, we characterized the temperature-dependent increase as having spectral features similar to that of prompt fluorescence but with a lifetime identical with that of the phosphorescence. In a word, it seemed to have the characteristics one would predict for thermally activated delayed fluorescence, and consequently we attribute the small rise in short wavelength emission at higher temperatures to an increased amount of delayed fluorescence.

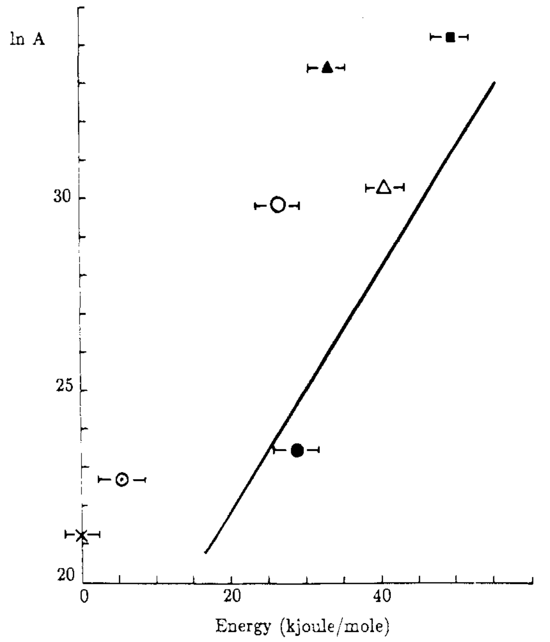

Figure 3. Barclay–Butler plot for doublet decay: (×) $[Cr(urea)_6]^{3+}$; (⊙) $[Cr(ox)_3]^{3-}$; (▲) $[Cr(NCS)_6]^{3-}$; (○) *trans*-$[Cr(NH_3)_2(NCS)_4]^-$; (●) *trans*-$[Cr(en)_2(NCS)_2]^+$; (△) $[Cr(en)_3]^{3+}$; (■) *trans*-$[Cr(py)_4F_2]^+$. The line is from ref 11; data points are taken from Table I.

In $[Cr(urea)_6]^{3+}$, and $[Cr(ox)_3]^{3-}$, for which prompt fluorescence had not previously been documented, we were also able to detect immediate (<100 ps) weak fluorescence in the regions where such emission would be expected to occur. In these two molecules we also observed emission that we attribute to delayed fluorescence.

Unfortunately, the delayed fluorescence is so close to the limit of detectability that we were unable to evaluate the delayed fluorescence yield as a function of temperature with sufficient precision to determine an activation energy for its appearance. We were, however, able to make a qualitative observation of this delayed fluorescence increasing at higher temperatures in each molecule we studied except *trans*-$[Cr(en)_2(NCS)_2]^+$, $[Cr(en)_3]^{3+}$, and *trans*-$[Cr(py)_4F_2]^+$.

Finally, in Figure 3 we reconstruct the Barclay–Butler plot of Zinato and co-workers.[11] Our data points are shown along with their line of best fit to their data.

Discussion and Conclusions

It is our objective here to establish whether RISC is ever important and, if so, to identify the boundary between the cases in which RISC dominates and those in which another process is lifetime controlling.

The correlation evident in Table I between our measured values of the energy of activation, E_{meas}, and the values predicted by the FAS model, E_{FAS}, provides good support for the hypothesis that RISC from the doublet to the excited quartet is the mechanism that is lifetime limiting until the energy gap reaches about 35 kJ mol^{-1}, at which point a different process becomes dominant.

Another point of evidence in support of RISC is the detection of luminescence, which is most plausibly identified as delayed fluorescence from molecules that return from the metastable doublet to the excited quartet state. It is noteworthy that the

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luminescence we assign to delayed fluorescence was not observed in the three cases in which the energy barrier is largest, for which return to the quartet either would not occur at all or would occur so rarely that any delayed fluorescence would be below the limit of detectability. The observation of delayed fluorescence tempts one to think of rapid equilibration between the excited quartet and the phosphorescent doublet. As discussed further below, we do not have any evidence that there is a thermally equilibrated excited quartet, so we do not speak of an electronically equilibrated quartet either. We do not know the ratio of intersystem crossing rates to decay rates for the excited quartet.

As a corollary, the applicability of the FAS model itself is supported. Agreement for the octahedral complexes is better than for complexes that are distorted from octahedral. Even the latter fall generally within the range expected. Furthermore, the discrepancies that exist in those cases are considerably reduced from what appears in Table I, if one introduces approximate corrections for the deviations from octahedral symmetry. These were worked out in another place.[22] Additional detail is becoming available for a wider variety of complexes about the states existing in ambient solutions. For example, it has been reported that the ordering of the doublet states in quadrate Cr(III) complexes changes with solvent.[23] One of our systems, *trans*-$[Cr(py)_4F_2]^+$ has the atypical, inverted ordering. The FAS model does not address such details.

The present work agrees with an earlier study,[16] based on a quite different approach, in concluding that the lifetime of the lowest doublet state varies inversely with the energy separation between the lowest doublet and the excited quartet for energy gaps up to some limit.

As a further test of whether there is a common decay mechanism for doublets in all Cr(III) compounds, consider the Barclay–Butler plot of Figure 3. It is evident that the correlation noted previously[11] for the long-lived species is destroyed when the short-lived complexes are included in the analysis. One must conclude that there are at least two important decay mechanisms, one of which dominates for the long-lived species and the other for the short-lived species. The former exhibits an activation energy that is never too far from 40 kJ mol,$^{-1}$ while the latter shows an activation energy that correlates reasonably well with estimates for the barrier to RISC.

What is the significance of the limiting value of 35–40 kJ mol^{-1} for the activation energy of the lifetime-limiting process in the lowest doublet? It might conceivably mean that there is some direction in the multidimensional coordinate space in which a barrier between doublet and excited quartet has a constant value of that magnitude, despite the fact that the spectroscopic energy separation has no such limit. More likely, however, is the common suggestion that there is some process in the doublet itself which sets that limit, as has been assumed throughout this paper. This process may be taken to be photochemistry, although that term would need some elucidation. It may be better to think of a more generalized curve crossing.

Although we have considered "a limit" to the measured activation energy from the point of view of RISC losing out to a competitive process, we must now stress that the "limit" is not a unique value. Rather, the range of activation energies attributed to the "photochemical" process extends over a factor of 2.[9-11] While still quite small, that may be large enough to support correlations with some parameter governing such processes, as has been discussed in those reports.

We also point out that the very strong ligand field instances ($Cr(CN)_6^{3-}$ and the polypyridyl complexes) have always been considered to be unlikely candidates for control of doublet lifetime by RISC. If the regime of domination by "chemical reaction" is reached already with the compounds treated in this paper, one would expect that those very strong field cases would fall also within that class. Since we are aware of no serious dispute in that area, we have not reviewed the substantial and convincing literature.

Finally, we would remark that RISC itself is also somewhat ill-defined if, as now seems possible, a thermally relaxed quartet does not exist.[24] It may be well to think in terms of a multidimensional potential surface having saddlepoint barriers in several directions. Then the terms "reverse intersystem crossing" and "photochemical reaction" are attempts to label particular saddlepoints in ways that are useful for correlating patterns of behavior observed in different molecules over a range of conditions, but the terms should not automatically carry all the connotations they have in other branches of photophysics.

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Registry No. $[Cr(urea)_6]^{3+}$, 15276-06-9; $[Cr(ox)_3]^{3-}$, 15054-01-0; $[Cr(NCS)_6]^{3-}$, 15276-09-2; *trans*-$[Cr(NH_3)_2(NCS)_4]^-$, 16248-93-4; *trans*-$[Cr(en)_2(NCS)_2]^+$, 29845-02-1; $[Cr(en)_3]^{3+}$, 15276-13-8; *trans*-$[Cr(py)_4F_2]^+$, 47514-84-1.

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Heterobinuclear Transition-Metal Complexes. Synthesis and Optical Metal to Metal Electron Transfer

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Binuclear mixed-valence transition-metal complexes have been investigated extensively during the last 15 years.[1-6] Usually these mixed-valence compounds contain one metal in two different oxidation states connected by a bridging ligand. Such homobinuclear complexes are characterized by low-energy metal to metal charge-transfer (MMCT) absorption bands that are assigned to an electronic transition from the reducing to the oxidizing metal. Most investigations were carried out with Ru(II)/Ru(III) complexes.[1-5]

In a more general sense the concept of mixed-valence compounds can be extended to heterobinuclear complexes that contain different metals as reducing and oxidizing centers.[7] Due to the redox asymmetry of such systems MMCT bands are shifted to higher energies and occur frequently in the visible region. In many cases bridging ligands such as pyrazine were used to facilitate the inner-sphere metal–metal interaction.[1-5] These ligands are not well suited to observe MMCT absorptions in the visible region because CT transitions from the reducing metal to the bridging ligand (MLCT) occur in the same energy range. Intense MLCT bands may then hide or obscure MMCT absorptions. Cyanide as bridging ligand avoids these complications since MLCT transitions involving this ligand do not occur at low energies.[8]

In 1975 we started to investigate cyanide-bridged heterobinuclear mixed-valence compounds with particular reference to their

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