

1, the difference spectrum at zero delay indicates a blue shift in the absorption spectrum relative to the ground state.¹³ This would bring the laser wavelength into better resonance with the absorption maximum, an effect that might account for the stronger signal seen for the excited-state bands at pH 1.5 (Figure 2) despite the shorter lifetime of the protonated excited state.

The observation that the excited-state RR bands at pH 7 are superpositions of two spectra, one of which shows frequencies that are the same as are observed at pH 1.5, implies that some of the excited-state molecules are protonated even at pH 7. Certainly the excited state is expected to be more basic than the ground state, since protonation neutralizes the charge produced at the terminal N atom in the excited state (Figure 4). This stabilization is reflected in the red shift of the absorption maximum from 480 nm at pH 7 to 570 nm at pH 1.5. This wavelength shift can be used to estimate the excited-state pK_a shift²³

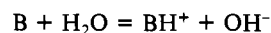
$$\Delta(pK) = 0.00209(\bar{\nu}_B - \bar{\nu}_{BH^+})/\text{cm}^{-1}$$

via the Förster cycle,²⁴ in which the difference in the ground- and excited-state protonation free energies is assumed to be given by the difference in the S_1 - S_0 energy gaps for the protonated and unprotonated forms. (The assumption in this equation that the difference in the 0-0 energies is given by the difference in the absorption maxima introduces a significant uncertainty.²³) For I and IH^+ the absorption frequency difference is 3300 cm^{-1} , giving an estimated $\Delta(pK_a)$ of 6.9. When added to the pK_a of the ground state, 4.5,¹³ this gives an excited-state pK_a of 11.4. Thus essentially all of the excited molecules are expected to be protonated at equilibrium.

It is unclear, however, what fraction of the molecules become protonated within the very short lifetimes of the excited states.

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At equilibrium, the ratio of the forward, k_f , and reverse, k_r , rate constants for the protonation reaction



must give the equilibrium constant

$$K_B = 10^{-14}/10^{-11.4} = 10^{-3.6} = k_f/k_r$$

The maximum value of k_r is the diffusion-controlled rate constant $\sim 10^{10}\text{ M}^{-1}\text{ s}^{-1}$, and consequently the maximum value of $k_f = \sim 10^{10}K_B = 10^{6.4}\text{ s}^{-1}$. With this rate constant, less than 0.1% of the initially excited molecules are expected to be protonated within even the longer of the two pH 7 lifetimes, 230 ps. Equilibrium conditions, however, are not expected to apply to the initially excited species, since the solvent cage is that appropriate for the ground state. It is likely that some of the excited molecules find themselves with H-bonded water molecules that are well positioned for proton transfer. Other examples of very fast excited-state proton-transfer reactions have been noted. For example, in a study of 2-naphthol fluorescence decay, Ofran and Feitelson²⁵ were forced to assume that some of the naphthol was deprotonated in the initially excited S_1 state in order to explain their data. Heterogeneity is evident in the excited I population at pH 7 from the finding of two lifetimes, both of which are attributable to the charge-transfer state.¹³ It is possible that the fraction with the short lifetime, 36 ps, is made up of those molecules that have undergone nonequilibrium proton transfer or else are sufficiently strongly H-bonded to have the same RR frequencies as protonated molecules.

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X-ray Photoelectron Spectra of Mixed-Valence Diruthenium Complexes. Distinguishing between Strongly and Weakly Interacting Metals in Delocalized Class III Complexes

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X-ray photoelectron (XP) spectra have been recorded for a series of trichloro-bridged diruthenium complexes containing the $[RuCl_3Ru]^{n+}$ ($n = 1-3$) fragment. Along with symmetrical and asymmetrical $[Ru(II),Ru(II)]$ and $[Ru(III),Ru(III)]$ complexes, the series contains both asymmetrical, mixed-valence class II complexes and a symmetrical, mixed-valence class III complex, $[As(p\text{-tol})_3]_2ClRuCl_3RuCl[As(p\text{-tol})_3]_2$ (**7**; $p\text{-tol} = p\text{-tolyl}$). Symmetrical $[Ru(II),Ru(II)]$ and $[Ru(III),Ru(III)]$ complexes give single Ru $3d_{5/2}$ peaks in accord with the chemically identical environments of the two ruthenium ions. Either one or two Ru $3d_{5/2}$ photolines are observed in spectra of asymmetrical $[Ru(II),Ru(II)]$ complexes depending on just how dissimilar are the ruthenium local environments. The trapped-valence, asymmetrical $[Ru(II),Ru(III)]$ complexes also yield one or two Ru $3d_{5/2}$ lines in their spectra, but in any case the lines are broader than the single Ru $3d_{5/2}$ line (full width at half-maximum 1.3 eV) observed for the symmetrical, average valence complex **7**. This result contrasts with previous XP spectra of Creutz-Taube-type class III complexes. Spectra of these complexes yielded two Ru $3d_{5/2}$ photoionization states of equal intensity split by 3.4-3.6 eV. In the Creutz-Taube-type complexes the unpaired electron originally equally shared between ruthenium centers in the ground state is stated to become localized on one or the other ruthenium under the influence of the Ru 3d core hole during photoemission. The absence of such splitting of the Ru $3d_{5/2}$ (and Ru $3p_{3/2}$) lines in the XP spectrum of **7** is consistent with much stronger electronic coupling between the two metal centers in this complex. It is estimated that whereas Creutz-Taube complexes have an electronic exchange parameter, α' , of 0.10 or less, this parameter must be greater than 0.9 for complex **7**.

Introduction

Over the past few years substantial effort has been expended¹⁻¹¹ assessing the degree of electron delocalization in mixed-valence dimetal complexes of general formula M^2M^{2+1} . Various spec-

troscopic measurements have been used to assign complexes to Robin and Day's¹² II (trapped valence) and III (average valence)

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Table I. Summary of XPS Data for Diruthenium Complexes

sample	classification	binding energies, eV ^a				
		Ru 3d _{5/2}	C 1s	Cl 2p _{3/2}	As 3d	P 2p
[Ru ₂ Br ₃ (PMe ₂ Ph) ₆]Br (1)	+2, +2; sym	280.9 (1.1) ^b	285.0	69.30, ^c 67.65 ^d		131.6
[Ru ₂ Cl ₃ (PEt ₂ Ph) ₆]Cl (2)	+2, +2; sym	281.0 (1.1)	285.0	198.75, ^c 197.0 ^d		131.5
(PEt ₂ Ph) ₂ CRuCl ₃ Ru(PEt ₂ Ph) ₃ (3)	+2, +2; asym	280.7 (1.5)	285.0	198.50 ^e		131.3
(PPh ₃) ₂ CRuCl ₃ Ru ₃ (CO)(PPh ₃) ₂ (4)	+2, +2; asym	281.9 (1.5), 280.9 (1.5)	285.0	198.7 ^e		131.8
(PPh ₃) ₂ ClRuCl ₃ Ru(CS)(PPh ₃) ₂ (5)	+2, +2; asym	281.9 (1.4), 280.9 (1.4)	285.0	198.7 ^e		131.8
(PPh ₂ Bz) ₃ RuCl ₃ RuCl ₂ (PPh ₂ Bz) (6)	+2, +3; asym	282.2 (1.5)	285.0	198.5 ^e		131.5
[As(<i>p</i> -tol) ₃] ₂ ClRuCl ₃ RuCl[As(<i>p</i> -tol) ₃] ₂ (7)	+2, +3; sym	280.9 (1.3)	285.0	198.9, ^c 198.0 ^d	43.8	
[As(<i>p</i> -tol) ₃] ₃ RuCl ₃ RuCl ₂ [As(<i>p</i> -tol) ₃] (8)	+2, +3; asym	281.0 (1.3), 281.9 (1.6)	285.0	198.9 ^e	43.8	
[As(<i>p</i> -tol) ₃] ₂ ClRuCl ₃ RuCl ₂ [As(<i>p</i> -tol) ₃] (9)	+3, +3; asym	282.30 (1.7)	285.0	198.95 ^d	43.9	

^a All binding energies referenced to a carbon 1s binding energy of 285.0 eV. Binding energies quoted are reproducible with a precision of ±0.1 eV.

^b Values in parentheses are full widths at half-maxima of Ru 3d_{5/2} lines. ^c Bridging halide. ^d Uncoordinated or terminal coordinated halide.

^e Bridging and terminal chlorides not resolved.

classifications. Initially, one technique thought to be capable of unambiguously distinguishing between the two classifications for a given complex was X-ray photoelectron spectroscopy (XPS).¹³ It was supposed that, on the XPS time scale (~10⁻¹⁷ s), mixed-valence class II complexes would give two different metal photoionization states while class III complexes would give only a single state. However, Hush¹⁴ subsequently showed on theoretical grounds that XPS should not necessarily be capable of distinguishing between class II and class III mixed valence dimetal complexes. According to the theory, even class III complexes can give two metal core level photoionization states. This is because the delocalized valence orbital is highly polarizable, so that under the influence of the localized metal core hole the unpaired electron associated with this orbital becomes trapped on one metal or the other and two final states are realized.

Consequently, one cannot infer from a spectrum giving two equally intense metal final states that the mixed-valence dimetal complex is a trapped-valence, class II complex. One of the most widely studied mixed-valence complexes, [(NH₃)₅Ru(pz)Ru(NH₃)₅]⁵⁺ (where pz = pyrazine), itself gives two equally intense metal core level photoionization states⁷ even though many other physical measurements indicate it is a class III complex. In this instance, and in all instances where two metal core level lines of equal intensity are observed, the XPS results are ambiguous; they cannot be used to classify the complex. However, the metal-metal interaction in [(NH₃)₅Ru(pz)Ru(NH₃)₅]⁵⁺ and related complexes is relatively weak, for the most part because of the large distance between metal centers. As the metal-metal interaction in class III complexes grows stronger, the metal core level spectrum must approach a single final state and the complex can be unambiguously classified as class III on the basis of the XPS result. Obvious examples of class III complexes with strong metal-metal interactions are the metal-metal-bonded complexes [Re₂X₄L₄][Y] (X = halide, L = neutral ligand, Y = BF₄⁻ or PF₆⁻), all of which have direct metal-metal bonds (2.25 Å).¹⁵ These complexes give single-state Re 4f_{5/2}, 4f_{7/2} XP spectra.^{16,17}

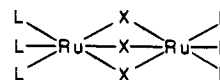
On the other hand, in Creutz-Taube-type complexes the ruthenium ions are separated by 6.9 Å or more by a ligand spacer.¹¹ There is then an absence of XPS measurements for mixed-valence

Table II. Summary of XPS Data for Reference Monoruthenium Complexes

	binding energies, eV			
	Ru 3d _{5/2}	C 1s	Cl 2p _{3/2}	P 2p
RuCl ₂ (PPh ₃) ₃	281.1 (1.1) ^a	285.0	198.2	131.7
mer-RuCl ₃ (PMe ₂ Ph) ₃	282.1 (1.5)	285.0	198.6	131.6

^a Values in parentheses are full widths at half maxima of Ru 3d_{5/2} lines.

dimetal complexes having metal-metal spacings between 2.3 and 7 Å. Somewhere in this gap, and very much dependent on the ligand bridging involved, the class III metal-metal interaction must switch from "weak" to "strong". One group of complexes that offers the opportunity to probe this regime is the class of complexes containing the [RuCl₃Ru]ⁿ⁺ (n = 1-3) core. These complexes have the general structure



where X is a bridging chloride or bromide and L is a terminal neutral (e.g. CO, PPh₃, etc.) or chloride anion ligand. In these complexes the Ru-Ru spacing is approximately 3.3 Å.¹⁸ Interpretation of XPS data for a variety of these complexes, and in particular the symmetric, mixed-valence [Ru(II),Ru(III)] complex [As(*p*-tol)₃]₂ClRuCl₃RuCl[As(*p*-tol)₃]₂, forms the basis of this study.

Experimental Section

All complexes were prepared by previously published procedures.¹⁹⁻²¹ Two ligand abbreviations used throughout the text are pz for pyrazine and As(*p*-tol)₃ for tri-*p*-tolylarsine.

X-ray photoelectron spectra were recorded with a Leybold Hereaus S-10 spectrometer using Mg Kα (1253.6 eV) X-radiation (240 W). Spectrometer pressure was typically (1-5) × 10⁻⁷ Pa during data collection. Some samples were simply crushed onto indium or copper wafers. More frequently, for improved spectral resolution and more useful peak intensities, samples were dissolved in distilled dichloromethane or acetone and one or two drops of each was placed on an aluminum or copper wafer. This technique produced excellent solvent cast films. In some cases this procedure was carried out in a Vacuum Atmospheres drybox with use of dried, distilled, degassed solvents. Once the solvent evaporated, the sample was transferred under inert atmosphere into a specially designed drybox for mounting onto the sample rod. Spectra were collected and processed with a Digital Specialties computer (Carrboro, NC). Core level binding energies are referenced to the carbon 1s line (285.0 eV), over 70% of the intensity of which is from the tertiary phosphine or arsine ligands. The spectrometer binding energy scale was calibrated in the manner described previously.²² Binding energies were

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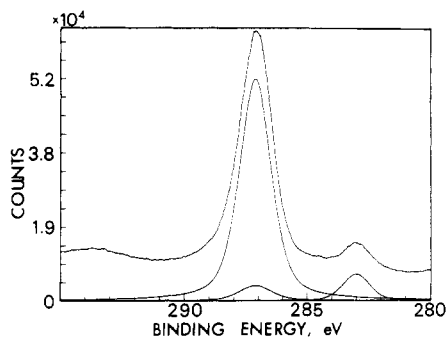


Figure 1. Experimental (upper) and deconvoluted (lower) X-ray photoelectron spectra of C 1s and Ru 3d_{3/2}, 3d_{5/2} lines for [As(*p*-tol)₃]₂ClRuCl₃RuCl[As(*p*-tol)₃]₂. In this and all subsequent experimental spectra shown, the spectrum in the figure is not corrected for sample charging (in this case 2.1 eV). In the simulated spectrum Ru 3d_{3/2}, 3d_{5/2} lines are constrained to have an area ratio of 2:3 and a splitting of 4.0 ± 0.1 eV. The broad feature centered around 294 eV in this and all other C 1s/Ru 3d spectra presented is a C 1s satellite from the group 5 (15²⁵) ligands.

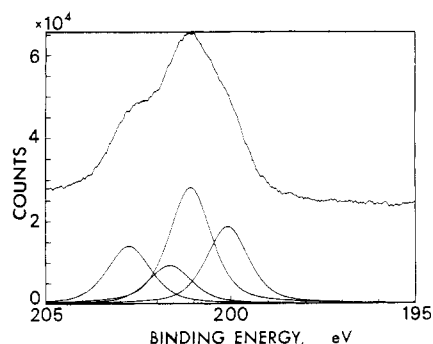


Figure 2. Chlorine 2p_{1/2}, 2p_{3/2} experimental (upper) and deconvoluted (lower) XP spectra of [As(*p*-tol)₃]₂ClRuCl₃RuCl[As(*p*-tol)₃]₂. The experimental spectrum shown is not corrected for sample charging. In the simulated spectrum each pair of chlorine 2p_{1/2}, 2p_{3/2} lines is constrained to have an area ratio of 1:2 and a splitting of 1.0 ± 0.1 eV.

typically reproducible within ±0.1 eV. Core level intensities were measured by numerical integration.

Results

The core level binding energies recorded for the diruthenium complexes investigated are summarized in Table I. Core level spectra were also recorded for the two monoruthenium complexes RuCl₂(PPh₃)₃ and RuCl₃(PMe₂Ph)₃. The XPS binding energies for these two complexes are summarized in Table II. The series of diruthenium complexes contains both symmetric and asymmetric [Ru(II),Ru(II)] and [Ru(II),Ru(III)] complexes, as well as an asymmetric [Ru(III),Ru(III)] complex. Due to the overlap of Ru 3d_{3/2}, 3d_{5/2} and C 1s lines and, in some cases, overlap of Cl 2p_{1/2}, 2p_{3/2} doublets from bridging and terminal halide ions, curve-fitting procedures were frequently utilized to accurately assess ligand and metal peak binding energies, widths, and intensities. These procedures, along with measurements of core level peak intensities to check sample stoichiometries, helped to determine whether sample decomposition had occurred. Examples of deconvoluted spectra are shown in Figures 1–5.

Along with the Ru 3d spectra recorded for all the complexes, ruthenium 2p_{3/2} spectra were also recorded for selected complexes, including samples 4 and 7. The Ru 2p_{3/2} lines are very broad (fwhm 3.0–3.6 eV), as expected (Coster–Kronig broadening), but the lines are useful because they allow comparisons of Ru line intensities uncomplicated by overlaps with other lines and also allow detection of exceptionally large (greater than 2 eV or so) metal core level splittings, if any are present.

Replicate spectra were recorded for most samples to further assess whether sample decomposition had taken place during XPS

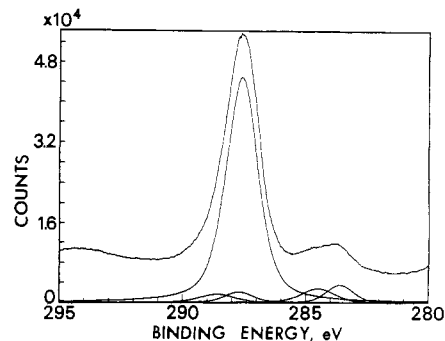


Figure 3. Experimental (upper) and deconvoluted (lower) X-ray photoelectron spectra of C 1s and Ru 3d_{3/2}, 3d_{5/2} lines for [As(*p*-tol)₃]₃RuCl₃RuCl₂[As(*p*-tol)₃].

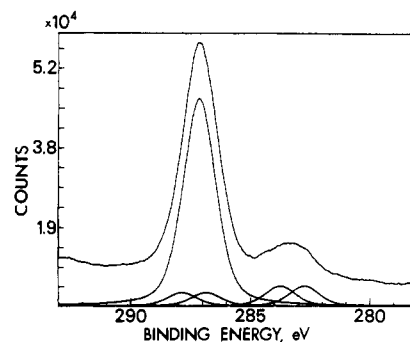


Figure 4. Experimental (upper) and deconvoluted (lower) X-ray photoelectron spectra of C 1s and Ru 3d_{3/2}, 3d_{5/2} lines for (PPh₃)₂ClRuCl₃Ru(CO)(PPh₃)₂. In the deconvoluted spectrum the Ru 3d_{3/2}, 3d_{5/2} lines are constrained to have an area ratio of 2:3 and a splitting of 4.0 ± 0.1 eV.

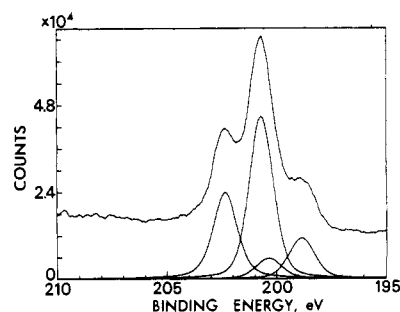


Figure 5. Experimental (upper) and simulated (lower) chlorine 2p_{1/2}, 2p_{3/2} XP spectra of [(PEt₂Ph)₃RuCl₃Ru(PEt₂Ph)₃]Cl. Again, in the simulated spectrum each pair of Cl 2p_{1/2}, 2p_{3/2} lines is constrained to have an intensity ratio of 1:2 and a splitting of 1.0 ± 0.1 eV.

measurements. Two samples susceptible to decomposition were 4 and 7. Since data for 7 are central to this study, exceptional care was taken to ensure that the data reported here are accurate. Steps taken include recording and storing data as a function of irradiation time and preparing the sample for analysis in a drybox (≤1 ppm H₂O) with use of degassed, freshly distilled solvents (acetone and dichloromethane). These steps resulted in reproducibly recording spectra of 7 such as those shown in Figures 1 and 2. For the pure complex we record a narrow Ru 3d_{5/2} line (fwhm 1.3 eV) and obtain a good fit of the experimental Cl 2p envelope with two sets of Cl 2p_{1/2}, 2p_{3/2} lines, one set for the lower binding energy terminal chloride ligands and the other for the higher binding energy bridging chloride ligands, with the two sets having the appropriate 2:3 intensity ratio.

As expected, metal binding energies generally increase with increasing ruthenium oxidation state. Ruthenium 3d_{5/2} full widths at half-maxima are typically between 1.1 and 1.7 eV. Narrower lines are recorded for RuCl₂(PPh₃)₃ and most of the symmetric [Ru(II),Ru(II)] complexes. Broader lines are a consequence of either chemical inequivalence of ruthenium sites or simply un-

resolved multiplet splittings associated with the Ru(III) ($\text{spin } 1/2$) 3d photolines. On the basis of comparisons of spectra for monometal and symmetric, isoivalent dimetal complexes with those of unsymmetric or nonisoivalent complexes, it was concluded that the broadened Ru 3d_{5/2} photolines recorded for the two complexes (PPh₃)₂ClRuCl₃Ru(CX)(PPh₃)₂ (X = O, **4**; X = S, **5**) and the asymmetric [Ru(II),Ru(III)] complex [As(*p*-tol)₃]₃RuCl₃RuCl₂[As(*p*-tol)₃] (**8**) should be deconvoluted. The Ru 3d/C 1s spectra for samples **4** and **8** are shown in Figures 3 and 4.

Ruthenium 3d spectra from other complexes were either not broadened sufficiently or overlapped with the C 1s line too much to warrant curve deconvolution.

In all instances except sample **7**, already described above, bridging and terminal halide ligand lines were not resolved sufficiently to warrant curve deconvolution. The only other complex halide spectra that obviously contained resolvable lines from different halide ion environments were those for [Ru₂X₃(PR₂Ph)₆]X (X = Br, **1**; X = Cl, **2**). An example of the Cl 2p spectrum typically recorded for **2** is shown in Figure 5. As expected, the binding energy of the uncoordinated anion is substantially lower than that of the doubly coordinated anions.

Discussion

As mentioned in the Introduction, the focus of this work is to assess whether the class III mixed-valence complex [As(*p*-tol)₃]₂ClRuCl₃RuCl[As(*p*-tol)₃]₂ (**7**) contains weakly or strongly interacting metal centers in the XPS sense as illustrated by Hush.¹⁴ Two equations derived by Hush¹⁴ and modified by Citrin and Ginsberg⁷ summarize the behavior expected for metal XP spectra of class III mixed-valence dimetal complexes. These equations are

$$\alpha = 2J'/\delta \quad (1)$$

$$\frac{I_+}{I_-} = \left[\frac{1 + (\alpha^2 + 1)^{1/2} + \alpha}{1 + (\alpha^2 + 1)^{1/2} - \alpha} \right]^2 \quad (2)$$

The unitless parameter α is a measure of electronic coupling of the two metal centers, where J' is the electronic coupling integral during photoionization (J' is always less than J , the corresponding integral for the undisturbed molecule) and δ is the energy difference between the two photoionization states as measured experimentally. In eq 2 I_+ is the intensity of the lower binding energy peak while I_- is the intensity of the higher binding energy peak. From these equations one can see that increased metal-metal coupling results in increased partitioning of signal intensity into the lower binding energy peak, I_+ , and, generally, in decreased core level splittings. As we have noted, in the strong-interaction limit the peaks coalesce into a single narrow peak. Practical and theoretical considerations indicate that class III complexes with $\alpha \leq 0.10$ will give metal core level XP spectra that are indistinguishable from spectra of class II complexes (i.e. two metal core level peaks of approximately equal intensity). While eq 1 and 2 apply only to the interpretation of the metal spectrum of sample **7**, the metal spectrum of this sample is most reliably interpreted not only by the equations but also in the context of how its spectrum is related to those of very similar complexes.

All the other mono- and diruthenium complexes (based on the [RuCl₃Ru]ⁿ⁺ ($n = 1-3$) core) included in this study provide the opportunity to examine the effects of systematic variation of metal oxidation state and ligand coordination environment on the Ru 3d spectra.

The simplest metal spectra recorded are for the monometal complexes RuCl₂(PPh₃)₃ (**10**) and RuCl₃(PMe₂Ph)₃ (**11**) and the symmetric, homovalent diruthenium complexes ([Ru(II),Ru(II)]). These spectra provide data for peak binding energy, shape, and intensity analysis without the complications of metal-metal interactions. Next we consider the spectra for the mixed-valence asymmetric class II diruthenium complexes and finally the spectrum of the mixed-valence symmetric diruthenium complex **7**.

The two monoruthenium complexes **10** and **11** examined give single Ru 3d_{5/2} lines, with that of the diamagnetic Ru(II) complex **10** narrower by 0.3 eV than that of the paramagnetic Ru(III) complex **11** (fwhm 1.1 and 1.4 eV, respectively). The metal binding energy difference between the two complexes is of the expected sign but is about 0.4 eV greater than that predicted by using the ligand group shift model.²³

The five [Ru(II),Ru(II)] complexes **1-5** examined give one or two Ru 3d doublets depending only on the local coordination environment about each ruthenium. For the symmetrical [Ru(II),Ru(II)] complexes **1** and **2** a single narrow Ru 3d_{5/2} line (fwhm 1.1-1.2 eV) is found. The three asymmetrical [Ru(II),Ru(II)] complexes **3-5** give broader Ru 3d_{5/2} lines. In the case of complexes **4** and **5** the Ru 3d_{5/2} lines are broad enough to warrant curve deconvolution into two Ru 3d_{5/2} lines of equal intensity. The two deconvoluted Ru 3d_{5/2} lines are separated by 1.0 eV. On the basis of considerations of ligand effects on metal binding energies²³ the higher binding energy Ru 3d_{5/2} peak is assigned in each case to the Ru center to which CO (**4**) or CS (**5**) is bound. As with the monoruthenium(III) complex RuCl₃(PMe₂Ph)₃, the asymmetric diruthenium(III) complex **9** gives broadened but symmetric Ru 3d lines (fwhm 1.7 eV) indicative of either a single or two indistinguishable ruthenium environments. For both Ru(III) complexes **9** and **11** the lines are broader because of unresolved multiplet splittings that arise during photoemission as a consequence of coupling of the unpaired valence electron with the unpaired core electron. Additional incremental broadening of the metal line in the spectrum of **9** might also be expected but is not detected, due to the inequivalent metal environments. As expected, the Ru 3d_{5/2} binding energies for these complexes are about 1 eV higher than those recorded for the Ru(II) complexes.

Two asymmetric, class II [Ru(II),Ru(III)] complexes (**6**, **8**) were examined. These asymmetric complexes ought to give two Ru 3d doublet spectra corresponding to the two chemically different Ru centers. Both spectra are broadened, but only that of **8** is broadened sufficiently (fwhm 1.9 eV) to warrant deconvolution (Figure 3). The Ru 3d_{5/2} envelope is skewed such that the higher binding energy component is flatter and broader. The broader, higher binding energy line is from the (trapped-valence) Ru(III) center having the coordination environment (μ -Cl)₃RuCl₂[As(*p*-tol)₃]₃, while the narrower, lower binding energy line is from the Ru(II) center with the coordination environment [As(*p*-tol)₃]₂ClRu(μ -Cl)₃. These assignments necessarily follow from the discussion above.

The only symmetrical, mixed-valence [Ru(II),Ru(III)] complex examined, [As(*p*-tol)₃]₂ClRuCl₃RuCl[As(*p*-tol)₃]₂ (**7**), gives a sharp (fwhm 1.3 eV) Ru 3d_{5/2} line, centered at 280.9 eV. The line width is comparable to those of diamagnetic, single-sited Ru(II) complexes. The observed binding energy is also comparable to those measured for the [Ru(II),Ru(II)] complexes **1-3** and so at first appears to be slightly low. However, the lower binding energy is likely due to the unusual, larger relaxation energy²⁴ afforded this complex during photoemission (or, in the framework of the Hush model, a high percentage of total photoemission intensity is invested in I_+ ; see eq 2).

It appears then that this mixed-valence complex yields a single Ru 3d_{5/2} photoemission line. However, due to interference from the C 1s line, it is possible that we cannot see a second Ru 3d_{5/2} line in the spectrum of **7**. If this is so, then either the second, higher binding energy peak is strong and the splitting between the two peaks is greater than 2 eV or the second, higher binding energy Ru 3d_{5/2} line is very weak (no more than 20% of the

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(25) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III \rightarrow 3 and 13.)

intensity of the main line) and is lost in the base line. If a hidden higher binding energy peak were comparable in intensity to that of the lower binding energy peak, then the Ru 3d_{5/2} intensity derived from the deconvoluted spectrum shown in Figure 1 would be anomalously low compared with that of other complexes while the C 1s line intensity would be anomalously high. Furthermore, the large Ru 3d splitting required to hide the high-binding-energy Ru 3d peak under the C 1s line ought to be observable even in the Ru 2p_{3/2} spectrum of the complex. We examined these possibilities by comparing Ru 3d_{5/2}/Cl 2p and Ru 2p_{3/2}/Cl 2p intensity ratios recorded for **7** with those of all the other ruthenium chloride complexes. The Ru 3d_{5/2}/Cl 2p and Ru 2p_{3/2}/Cl 2p intensity ratios for **7** are both within 20% (albeit on the low side of all but one) of all other measured ratios. The Ru 2p_{3/2} line width for **7** is normal. Given experimental errors, we find then that at least 80% of the Ru 3d_{5/2} intensity expected from two ruthenium centers in **7** is accounted for in the deconvoluted spectrum. Consequently, the metal XP spectrum of **7** is consistent with that of a strongly delocalized class III complex. For such a complex a large portion of the total metal core level photoemission intensity resides in a single, low-binding-energy line. From the quality of the spectrum we estimate, using eq 2, that the electron exchange parameter α for **7** must be greater than 0.9.

Conclusions

The diruthenium complexes examined have provided the opportunity to systematically assess the effects of ligand coordination

environment, metal oxidation state, and metal–metal interaction on the metal XP spectra. One complex is of particular interest in this series; the symmetric, mixed-valence [Ru(II),Ru(III)] complex [As(*p*-tol)₃]₂ClRuCl₃RuCl[As(*p*-tol)₃]₂. Depending on the strength of the metal–metal interaction, the metal XP spectrum from this complex could give any results along the continuum from two equally intense metal lines separated by 1 eV or more, to unequal intensities from the two lines with the lower binding energy line “stealing” intensity from the higher binding energy line, to a single, narrow metal line (indistinguishable metal centers). The spectrum observed is a function of the extent of unpaired electron delocalization during photoemission. It was found that, to the degree of resolution possible, this complex gives a metal spectrum in which at least 80% of the metal signal is present in a single, low-binding-energy final state. This experimental result reflects more extensive unpaired electron delocalization in this complex compared with that in the Creutz–Taube complex [(NH₃)₅Ru(pz)Ru(NH₃)₅]⁵⁺, which gives two well-separated metal lines of equal intensity. We estimate the value of α in **7** is greater than 0.9, whereas in the Creutz–Taube complex it is less than 0.10. This work, combined with Hush’s theory, suggests that very unusual metal XP spectra ought to be obtained from class III mixed-valence complexes having metal–metal spacings between 3.5 and 6 Å.

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Spectral Study of Tris(β -dionato)cobalt(III) Chelates. Structure–Redox Potential Relations

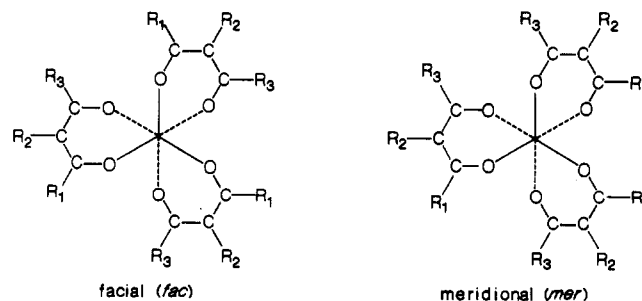
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A series of 16 tris(β -dionato)cobalt(III) chelates have been prepared, and their infrared and solution electronic spectra were obtained. Evidence is provided that substituents within the β -dionato moiety induce electronic effects influencing the electronic structure, bonding characteristics, and stability of these complexes while they barely affect the ligand field parameter Dq . The influence of the substituents on the chelate ring electron density is primarily inductive in nature, and the parameters best describing this influence are Hammett σ functions. It was found that electron-attracting groups weaken the Co–O bond and strengthen the C=O and C=C bonds in the chelate ring, the stretching frequencies of which are linearly dependent on Hammett σ functions. Similarly dependent are the polarographic reduction potentials of these low-spin chelates and the energies of the frontier molecular orbitals. The experimentally determined energies of the HOMO and LUMO orbitals are in excellent agreement with previously computed values. The linear dependence encompasses the energy of the first charge-transfer transition assigned to a $\pi^* \leftarrow t_{2g}$ excitation.

Introduction

The chelates of β -dione compounds constitute a very important class of complexes. Their tremendous versatility is attested to by the fact that they have been coordinated to a great variety of metals and metalloids.^{1–3} Coordination takes place through the carbonyl oxygen atoms, and with trivalent metals the oxygen may be thought of as occupying the apices of a slightly distorted octahedron.⁴ The symmetric β -diketonates afford optical isomers⁵ whereas Claisen condensation offers the possibility of forming asymmetric β -dione compounds that can be used for the preparation of geometrical isomers (facial and meridional) in addition to the optical isomers.^{4,6} The number of such compounds can be extended even more to encompass complexes with specific groups since the β -diketonato chelates exhibit “quasi-aromatic”



character and many electrophilic substitution reactions have been effected at the methinic carbon atom of the chelate ring.^{7,8} In this way a series of complexes can be prepared in order to investigate the influence of various substituents on the spectral characteristics and other physical properties of this class of compounds.^{9,10}

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