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Photoelectron Spectra of Dithiaspirocyclobutane Molecules. Electronic Spectra of Their Ruthenium Complexes and Evidence from CNDO/2 Calculations for a Hyperconjugating Electron-Transfer Mechanism

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Intervalence electron transfer was found to occur with surprising efficiency through the ruthenium dinuclear complexes based on the dithiaspiro bridging ligands 2,6-dithiaspiro[3.3]heptane (I), 2.8-dithiaspiro[3.1.3.1]decane (II), and 2,10-dithiaspiro[3.1.1.3.1.1]tridecane (III). It was found from CNDO/2 calculations that the highest occupied bonding molecular orbital of each molecule was ideally set up with p_z orbitals on the S and C atoms for "sideways π overlap", thus providing a hyperconjugating electron-transfer pathway between the ruthenium atoms bonded to the terminal sulfurs. The CNDO/2 calculations predict this hyperconjugating orbital to be the HOMO whereas photoelectron spectroscopy indicates that the HOMO is an almost degenerate set of orbitals largely comprised of a nonbonding pair in the p_x orbital of each sulfur atom. These nonbonding p_x orbitals are presumably used to form coordinate covalent bonds to the ruthenium atoms in the corresponding dinuclear complexes. The electronic spectra show ligand-to-metal charge-transfer bands in the visible region for either mononuclear or dinuclear ruthenium(III) complexes of the dithiaspiro ligands. The values of the highest energy visible transitions do not vary as the PES ionization energies of the appropriate orbital as ring number increases, indicating that the spiro ligands having an odd number of rings interact in a different manner with the metal atom than do those ligands having an even number of rings.

Introduction

In an earlier publication,[2a] we discussed the intervalence electron-transfer reactions between ruthenium atoms of complexes of the type $(NH_3)_5Ru^{II}$-S<>S-$Ru^{III}(NH_3)_5{}^{5+}$, where S<>S represents the dithiaspiro ligands denoted by I–III.


I


II


III

The electronic pathway was thought to involve a "through-bond" rather than a "through-space" interaction because of the large Ru–Ru distances involved (about 9–14-Å direct Ru–Ru distances over the three dinuclear complexes derived from ligands I–III). One of the questions that remained concerned the nature of the molecular orbitals involved in transferring the electron. There is some evidence[2b,3] that cyclobutane and heterocyclobutanes are capable of achieving additional electronic stability through hyperconjugation. The CNDO/2 calculations that we describe in the present work indicate in each case that the highest σ orbital of I–III is an almost pure hyperconjugating orbital and the apparently facile intramolecular electron-transfer reactions of the ruthenium dinuclear complexes derived from these ligands are probably the manifestation of a hyperconjugating electron-transfer mechanism. These calculations, in conjunction with the photoelectron spectra of the dithiaspiro ligands and the UV–vis spectra of the corresponding mononuclear and dinuclear complexes, have been used to explore the unusual electronic nature of these molecules.

Experimental Section

Chemicals and Reagents. All chemicals were reagent grade and were used as supplied. Solvents were purchased from Baker Chemicals, and $[Ru(NH_3)_6]Cl_3$ was obtained from Strem Chemicals. The oxidant $(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$ was purchased from G. Frederick Smith Chemical Co. The organic ligands were prepared, by following literature procedures,[4,5] by G.S. Thiacyclobutane was purchased from Aldrich Chemicals, and the NH_4PF_6 was obtained from Alfa Products.

Synthesis of (μ-2,8-Dithiaspiro[3.1.3.1]decane)decaamminediruthenium(II,II) Hexafluorophosphate, $[(NH_3)_5RuS_2C_8H_{12}Ru(NH_3)_5](PF_6)_4$, and ($\mu$-2,10-Dithiaspiro[3.1.1.3.1.1]tridecane)decaamminediruthenium(II,II) Hexafluorophosphate, $[(NH_3)_5RuS_2C_{11}H_{16}Ru(NH_3)_5](PF_6)_4$. These compounds were prepared and characterized as reported earlier.[2a]

Synthesis of (2,8-Dithiaspiro[3.1.3.1]decane)pentaammineruthenium(II) Hexafluorophosphate, $[(NH_3)_5RuS_2C_8H_{12}](PF_6)_2$, and (2,10-Dithiaspiro[3.1.1.3.1.1]tridecane)pentaammineruthenium(II) Hexafluorophosphate, $[(NH_3)_5RuS_2C_{11}H_{16}](PF_6)_2$. To a solution of 100 mg (2.02×10^{-4} M) of $[(NH_3)_5Ru(OH_2)](PF_6)_2$[6] in 3.0 mL of deaerated acetone was added 1.3 equiv of the ligand. The reaction was allowed to proceed for 2 h under a steady stream of acetone-saturated argon, after which time the solution was pale yellow. A yellow solid was then precipitated by addition of an excess of ether. This was filtered from the solution and was redissolved in a minimum of 0.1 M HCl. After the solution was refiltered, the supernatant was treated with solid NH_4PF_6 until a yellow precipitate again formed. It was filtered, washed with ether, and air-dried. The yield was about 40%. Anal. Calcd for $C_8H_{27}N_5F_{12}P_2RuS_2$: C, 14.81; H, 4.19; N, 10.80. Found: C, 14.43; H, 4.28; N, 11.06. Calcd for $C_{11}H_{31}N_5F_{12}P_2RuS_2$: C, 19.19; H, 4.54; N, 10.17. Found: C, 19.48; H, 4.68; N, 10.39.

Synthesis of (Thiacyclobutane)pentaammineruthenium(II) Hexafluorophosphate, $[(NH_3)_5RuSC_3H_6](PF_6)_2$. To a solution of 200 mg of $[Ru(NH_3)_5Cl]Cl_2$ in 5 mL of 0.18 M H_2SO_4 containing an excess of amalgamated zinc under an argon atmosphere was added 0.5 mL of the neat ligand. Acetone was then added dropwise until the cloud point was reached. The solution was stirred for 2 h and was then extracted three times with $CHCl_3$ to remove the excess organic material. Finally, solid NH_4PF_6 was added to the aqueous layer to precipitate a yellow solid in ~80% yield. Anal. Calcd for $C_3H_6N_5F_{12}P_2RuS$: C, 6.55; H, 3.85; N, 12.73; S, 5.83. Found: C, 6.93; H, 3.79; N, 12.07; S, 5.99.

Spectral Measurements. The UV–visible spectra were recorded on a Cary 17 spectrophotometer. All samples were dissolved in 0.10 M HCl prepared from triply distilled water. The photoelectron spectra were measured on a Perkin-Elmer PS-16 spectrometer and were calibrated by the simultaneous introduction of argon into the target chamber. The samples were heated until they became volatile and their spectra could be measured.

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(1) (a) Yeshiva University. (b) University of New Brunswick. (c) Phillips-Universität Marburg. (d) Queens College.

(2) (a) Stein, C. A.; Lewis, N. A.; Seitz, G. *J. Am. Chem. Soc.* **1982**, *104*, 2596. (b) Mollere, P. D. *Tetrahedron Lett.* **1973**, *29*, 2791.

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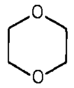
Electrochemical Measurements. The electrochemical cell was a conventional three-electrode type with an aqueous saturated calomel electrode (SCE) and with a platinum wire as the auxiliary electrode. The working electrode was a platinum button. All $E_{1/2}$ values are uncorrected for junction potentials. A PAR Model 173 potentiostat/galvanostat was used for potential control, and a PAR Model 175 universal programmer was used as a sweep generator for the cyclic voltammetric experiments. The PAR Model 176 was used as a current follower. Voltammograms were recorded on a Hewlett-Packard Model 7000 A X-Y recorder.

Method of Calculation. The molecular orbital calculations were performed with use of the CNDO/INDO program of Dobosh.[7] The closed-shell CNDO option was selected.

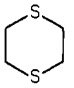
Analyses. Microanalyses were obtained from Schwarzkopf Microanalytical Laboratory, Woodside, NY 11377.

Results and Discussion

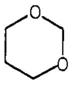
There has been considerable interest during the last few years in the interactions of equivalent orbitals in small molecules.[8,9] Sweigart and Turner,[10] in particular, have used the technique of photoelectron spectroscopy to ascertain the mechanisms by which equivalent lone-pair orbitals interact in small oxygen and sulfur heterocycles. They used qualitative overlap ideas and group theory to try to establish whether the lone-pair orbital splitting was due to through-space or through-bond interactions. In 1972 they concluded, from an analysis of the photoelectron spectra of several related small sulfur and oxygen heterocycles, that the lone-pair splitting of the heteroatoms was greater in sulfur when through space and greater in oxygen when through bond.[10] For example, the lone-pair splitting of 1,4-dioxane (IV) is 1.22 eV whereas that of 1,4-dithiane (V) is only 0.45 eV. Direct overlap of the lone-pair orbitals is likely to be small so the overlap is assigned to be of the through-bond type.



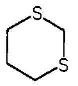
IV



V



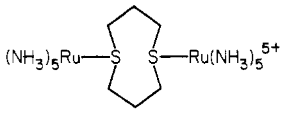
VI



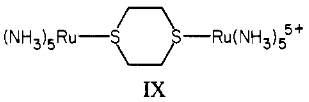
VII

In the meta systems (VI and VII), direct overlap of lone pairs is possible and the through-space splittings observed are 0.25 eV for 1,3-dioxane and 0.41 eV for 1,3-dithiane. In all cases, the highest occupied molecular orbitals were assumed to be the lone pairs on oxygen or sulfur, which are primarily p-type, essentially nonbonding orbitals.

The first indication that an intramolecular electron-transfer reaction could occur by a through-space mechanism came from the investigations of Stein and Taube[11] in 1978. Their study involved making a dinuclear ruthenium complex with 1,5-dithiocane as a bridging ligand (VIII). For comparison, they made the corresponding complex using 1,4-dithiane (V) as a bridge (IX). In this latter case, the electronic effects would be expected to be transmitted primarily through σ bonds although some slight overlap of the sulfur lone pairs may still occur. The 1,5-dithiocane dinuclear complex (VIII) showed significant through-space interaction between the sulfur atoms as manifested by a strong intervalence transition between the ruthenium atoms (λ_{max} = 1180 nm, ϵ_{max} = 75 M^{-1} cm^{-1} uncorrected for K_{com}). For the dinuclear complex based on 1,4-dithiane (IX), the interaction between ruthenium atoms was much weaker and the intervalence band was at higher energy (λ_{max} = 972 nm, ϵ_{max} = 6 M^{-1} cm^{-1}).



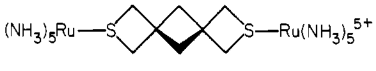
VIII



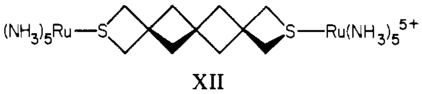
IX

In 1981, Stein and Taube[12] further reported an intervalence electron transfer through a bridging ligand of exclusively σ character in which the sulfur lone pairs could not overlap directly. The bridge that they selected was 2,6-dithiaspiro[3.3]heptane (I), giving the dinuclear complex X. A surprisingly intense intervalence transition was observed at 910 nm (ϵ = 43 M^{-1} cm^{-1}). We extended these studies[2a] to include the corresponding three-ring (II) and four-ring (III) spiro ligands, giving the ruthenium dinuclear complexes XI and XII. Intervalence transitions were observed at 808 nm (ϵ = 9 M^{-1} cm^{-1}) and 690 nm (ϵ = 2.3 M^{-1} cm^{-1}), respectively. The widths of the bands indicated that the transfer was nonadiabatic, and a tunneling formula was used to compute the rates of electron transfer between the ruthenium atoms in X–XII.[2a] The ability of these spiro bridges to mediate electron transfer had still not been explained in terms of the orbital pathways involved. We have now run the photoelectron spectra and have performed CNDO/2 calculations to explore the electronic nature of the spiro ligands I–III, which may be thought of as being based on the cyclobutane structure.

X



XI



XII

The photoelectron spectrum of cyclobutane itself was analyzed by Heilbronner et al.[13] in 1970. The ring is known to be puckered and has D_{2d} symmetry, as determined experimentally.[14] If the ring were planar, it would belong to the D_{4h} point group. Although the equilibrium geometry of the cyclobutane ring is puckered, Hoffmann[15] has reported that the degeneracies and orbital shapes of the planar D_{4h} model of cyclobutane were retained in the actual D_{2d} symmetry. His CNDO/2 calculations also showed retention of these features, as well as only small changes in eigenvalues upon flattening of the ring.

We have also assumed planar geometry in our calculations on the dithiaspiro ligands I–III since the equilibrium geometries of these molecules are unknown. By analogy to Hoffmann's results on cyclobutane, it is likely that puckering of the rings would introduce only minor changes in the calculations. For comparative purposes, we further assumed that all the molecules belong to the C_{2v} point group. In actual fact, the two- and four-ring spiro ligands (I and III) belong to D_{2d} and the three-ring ligand belongs to D_{2h}. The point group C_{2v} was selected to describe the symmetry of these molecules because it is a subgroup of both D_{2d} and D_{2h}.

The photoelectron spectra are reproduced in Figure 1 and ref 12, and the parameters are collected in Table I. The assignments of the transitions are made on the basis of the

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(8) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.
(9) Bischof, P.; Hashmall, J. A.; Heilbronner, E.; Hornung, V. *Tetrahedron Lett.* **1970**, 1033.
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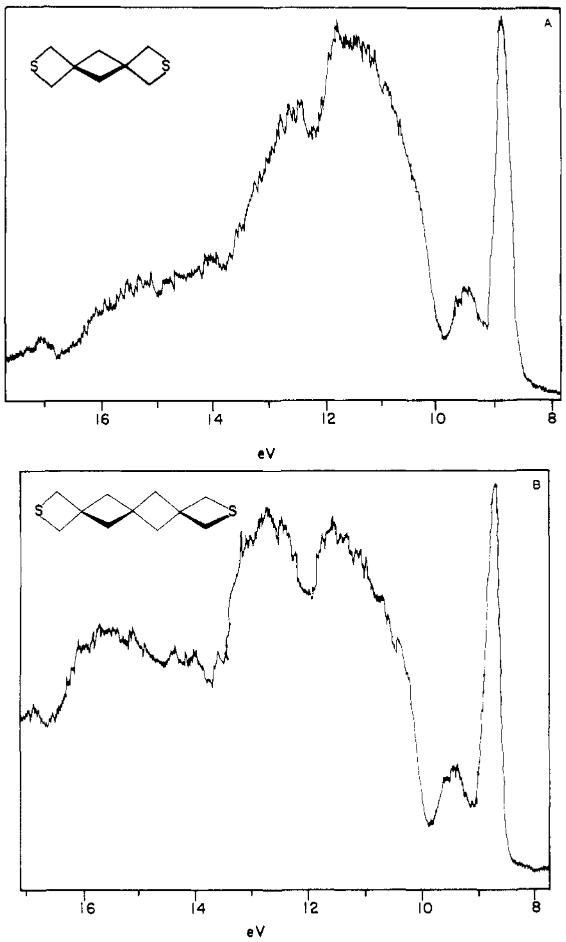

Figure 1. Photoelectron spectra of (A) 2,8-dithiaspiro[3.1.3.1]decane(II) and (B) 2,10-dithiaspiro[3.1.1.3.1.1]tridecane(III). There is about 1% delocalization of electron density into CH bonds that are adjacent to the sulfur atoms in each molecule. For the two-ring spiro molecule, about 8.3% of the electron density is found in the s, d_{z^2}, and $d_{x^2-y^2}$ orbitals on the sulfur atoms. This drops to 5.8% and 4.3% for the three-ring and four-ring systems, respectively.

Table I. Vertical Ionization Energies of Thia-Substituted Cyclobutane Derivatives[a]

compd	$IE_V(b_1)$, eV	$IE_V(a_1)$, eV	$IE_V(b_2)$, eV	ref
1-ring	8.65	10.60	11.89	*b*
	(9.97)	(10.70)	(11.90)	*c*
2-ring	8.71	10.04	12.00	*c*
	(10.11)	(9.71)	(11.96)	*c*
3-ring	8.75	9.45		*c*
	(10.00)	(9.41)		*c*
4-ring	8.75	9.55		*c*
	(9.97)	(9.24)		*c*

[a] Experimental results are listed. Calculated values are in parentheses. The calculated values have been scaled down by a factor of 1.17. [b] Reference 3. [c] This work.

CNDO/2 results. The greatest discrepancy in the prediction of ionization energies according to Koopmans' theorem is the calculation that the lone-pair ionizations (b_1) will be higher in energy than the a_1 values. The photoelectron spectra clearly indicate that ionizations of the sulfur lone pairs lie 0.70–1.95 eV lower in energy than those from any of the delocalized molecular orbitals. The scrambling of the σ/lone-pair ordering was earlier observed in the studies of Mollere and Houk[3] on simple four-membered ring heterocycles. They attributed the difficulty encountered between theory and experiment to the much greater electronic delocalization which occurs upon ionization of the localized b_1 lone-pair electrons as compared to that which occurs for the more localized a_1 orbital.

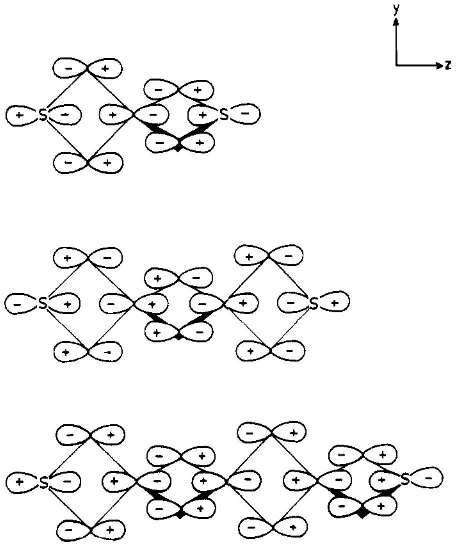

Figure 2. Representation of the highest occupied bonding orbitals of dithiaspiro molecules as determined by CNDO/2 calculations.

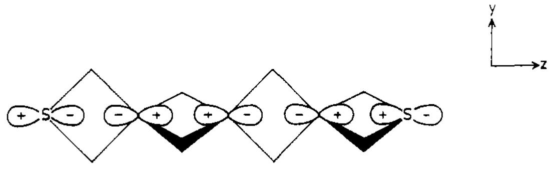

Figure 3. Representation of a hypothetical "through-space" pathway for electronic motion through a dithiaspiro molecule. There is no evidence from CNDO/2 calculations for such an orbital arrangement in the vicinity of the HOMO or LUMO.

The HOMO in each case must, then, be a nearly degenerate set of b_1 orbitals corresponding primarily to the lone pair on each of the sulfur atoms. These orbitals would be used to form coordinate bonds with the ruthenium atoms in the dinuclear complexes. The next lower molecular orbital of each of the dithiaspiro ligands is of a_1 symmetry. These are composed almost exclusively of p_z orbitals as shown in Figure 2 and are set up for "sideways π overlap", thus allowing a completely delocalized system to exist between the terminal sulfur atoms. It is particularly interesting to note that this "hyperconjugating electronic pathway" follows the molecular framework. Presumably this a_1 orbital may interact with the d orbitals on the ruthenium atoms of the corresponding dinuclear complexes, X–XII, thus providing an apparently rather facile electron-transfer mechanism as manifested by the intervalence transition bands of these complexes.[2a,12]

An alternative scheme that might be envisaged would have an orbital arrangement as shown in Figure 3. In this scheme, the electronic pathway would be "through space" rather than "through bond". Our CNDO/2 calculations do not, however, provide any evidence for such a through-space arrangement of orbitals anywhere in the vicinity of the HOMO's or the LUMO's of the dithiaspiro molecules (see Figure 4).

The a_1 orbital (HOMO) is not, of course, the only one that can contribute to the total wave function for electron transfer although, judging from its energy, it is probably the major charge carrier.[16] Figure 4 shows all of the molecular orbitals in the region of the HOMO and LUMO for the two-ring spiro ligand. The molecular orbitals 13, 14, 15, 23, 24, 30, and 31 may also contribute to the electron transfer, but the energies of these orbitals, particularly at the extreme ends of the series, would probably not be close enough to those of the metal 3d orbitals that significant overlap could occur.[16] It is unlikely

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(16) Larrson, S. *J. Am. Chem. Soc.* **1981**, *103*, 4034.

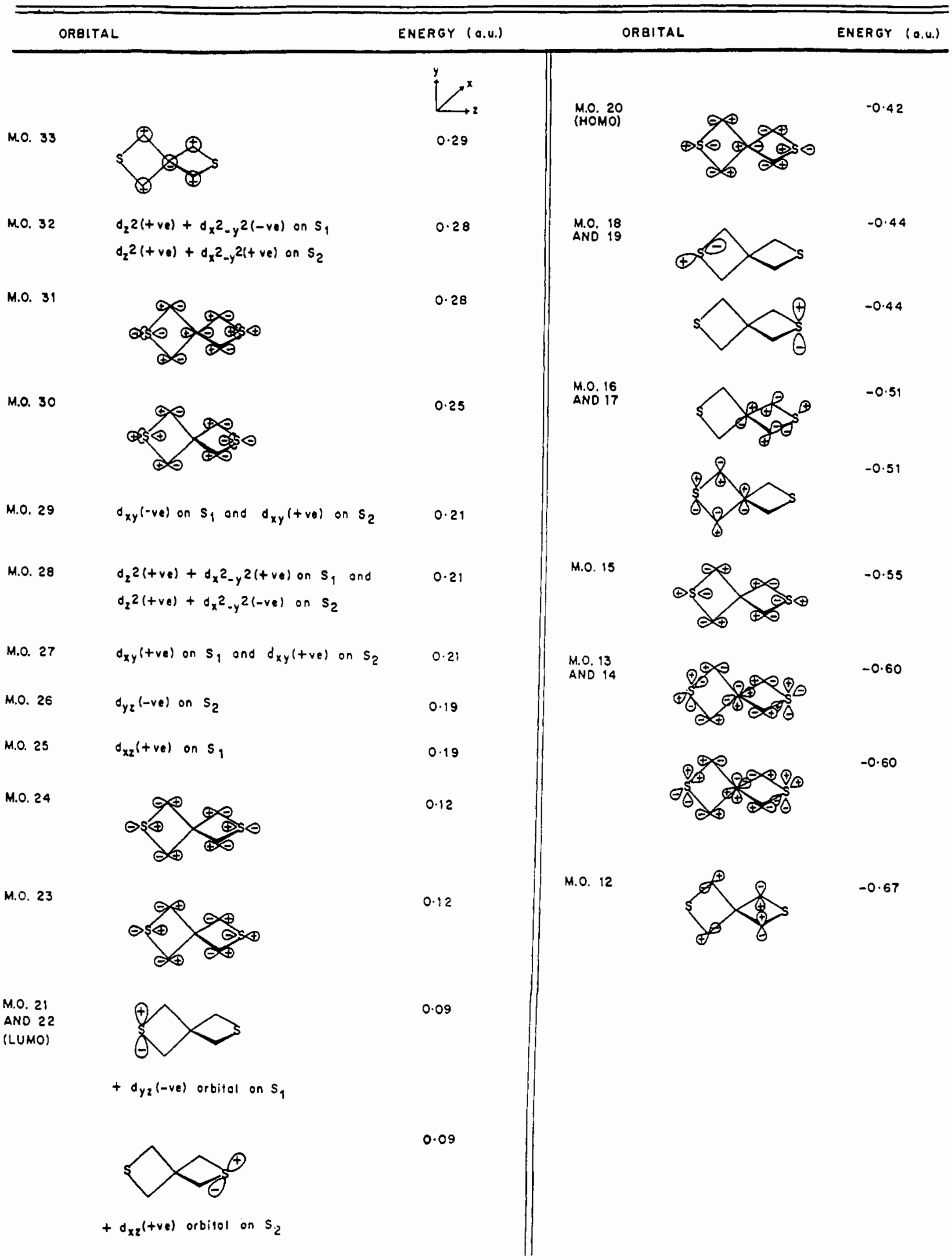


Figure 4. Molecular orbitals in the region of the HOMO and LUMO for the two ring spiro ligand.

that the b_1 orbitals (LUMO) make much of a contribution for two reasons. First, the b_1 orbitals are located at right angles to the direction of transfer, and second, both the MO calculations and the very sensitive photoelectron spectroscopic results indicate that there is no measurable interaction between the lone pairs on the sulfur atoms. Analogous arguments may be made for the three-ring and four-ring compounds.

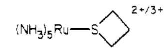
The question of which metal orbitals are involved in electron transfer cannot be absolutely determined. With the assumption of octahedral symmetry for the ruthenium atoms, the metal electrons are located in π orbitals and a π electron would have to transfer from the d^6 Ru(II) to a d^5 Ru(III) atom. The overlap of these metal d orbitals with the HOMO of the bridging spiro ligands cannot be good. However, the metal ions do not strictly possess octahedral symmetry so the division of the σ and π orbitals into e_g and t_{2g} sets is not absolute. Therefore, some mixing of the filled metal orbitals with the $d_{x^2-y^2}$ and d_{z^2} orbitals of the sulfurs in the HOMO may well occur. For the two-ring bridging ligand, about 6.82% of the electron density of the HOMO is concentrated in these d orbitals.

The electronic spectral parameters of the mononuclear and dinuclear complexes of ruthenium wiith the dithiaspiro ligands are given in Tables II and III. With both ruthenium atoms fully reduced, only ultraviolet transitions are observed which are MLCT in nature.[6] With at least one of the ruthenium atoms oxidized, ligand-to-metal charge-transfer bands appear in the visible region. In the case of the three- and four-ring spiro ruthenium complexes, two visible bands are observed. The lower energy ones arise from S(p) → Ru(π_d) LMCT transitions[11,12] whereas those at higher energy are likely $\sigma \rightarrow$ Ru(π_d) in nature. This latter transition is not observed in the

Table II. Electronic Spectral Parameters for Mononuclear Ruthenium Complexes of Dithiaspiro Ligands[a,b]

	λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1})[c]	
compd	Ru(II)	Ru(III)
1-ring	232 sh (2×10^3)	470 (290)
	286 (2.45×10^3)	
2-ring	282 (3.03×10^3)	458 (222)[d]
	270 sh ($\sim 2.8 \times 10^3$)	
3-ring	280 (3.10×10^3)	463 (223)
	245 sh ($\sim 2.3 \times 10^3$)	355 sh (~410)
4-ring	284 (3.09×10^3)	450 sh (~145)
	240 sh ($\sim 2.0 \times 10^3$)	389 (233)

[a] The complexes are of the type $(NH_3)_5Ru\text{-}S{<>}S^{2+/3+}$, where S<>S represents the dithiaspiro ligands I–III except for the one-ring complex, which is



[b] The spectral parameters for the 2-ring complex are taken from ref 11. All other values were determined in the present work.
[c] The medium used for taking the measurements was 0.01 M HCl unless otherwise noted. [d] The medium used for taking the measurements was 0.20 M HCl.

Table III. Electronic Spectral Parameters for Dinuclear Ruthenium Complexes of Dithiaspiro Ligands

	λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1})		
compd[a]	Ru(II, II)	Ru(II, III)	Ru(III, III)
2-ring[b]		910 (43)[g]	
	282 (7.80×10^3)[c]	452 (260)[d]	445 (488)[c]
	245 sh ($\sim 5.3 \times 10^3$)		
3-ring		808 (9)[g]	
	350 sh (775)[e,f]	462 (254)[d]	460 (492)[e]
	285 (6.8×10^3)[e]	335 sh ($\sim 1.1 \times 10^3$)[d]	345 (1.08×10^3)[e]
	245 sh ($\sim 4.7 \times 10^3$)[e]		
4-ring		690 (2.3)[g]	
	282 (5.88×10^3)[e]	460 sh (~300)[d]	455 sh (~465)[e]
	245 sh ($\sim 4.4 \times 10^3$)[e]	375 sh (~595)[d]	390 (790)[e]

[a] The complexes referred to are X–XII in the text. [b] The spectral parameters for the two-ring complex are taken from ref 11. All other values were determined in the present work.
[c] The medium used for taking the measurements was 0.2 M HCl.
[d] The medium used for taking the measurements was 0.24 M HCl.
[e] The medium used for taking the measurements was 0.1 M HCl.
[f] Ligand field transition. [g] IT transition.

Table IV. Electrochemical Properties of Ruthenium Spiro Complexes

ligand	mononuclear[a]	dinuclear[a]	ligand	mononuclear[a]	dinuclear[a]
1-ring	+515		3-ring	+515	+550
2-ring	+575	+600	4-ring	+510	+530

[a] All values are $E_{1/2}$ in mV vs. SHE (0.1 M HCl) and are reversible.

two-ring spiro ruthenium derivatives because its higher energy places it in the ultraviolet portion of the spectrum, where it is masked by other bands.

It is unclear why the PES ionization energies for the a_1 orbitals do not decrease monotonically as the number of rings increases. It may indicate that there is a difference in electronic communication between the sulfur atoms in the delocalized a_1 orbitals depending on whether an even or odd number of rings are present in the molecules. The same effect is observed in the LMCT transitions of the visible spectra.

Conversely, the intensities of the intervalence bands and the half-wave potentials of the two-, three-, and four-ring spiro ruthenium complexes (Table IV) do decrease monotonically throughout the series. This correlates with the calculated electron densities on the sulfur atoms, which also decrease as the number of rings increases, as expected.

Conclusion

The surprisingly rapid intramolecular electron transfer calculated to occur between ruthenium atoms in the dithiaspiro-bridged dinuclear complexes X–XII[2a] can be explained if the electron is mainly transferred by the highest occupied bonding molecular orbital. This orbital is set up to provide a conducting pathway across the entire bridge with "sideways π overlap" of p_z orbitals on the carbon and sulfur atoms. The fact that adjacent rings are oriented perpendicularly to each other is unimportant in these molecules since a p_z lobe on the bridgehead carbon atom is always in the plane of the ring on either side of this carbon. There is no evidence for any molecular orbital close to a HOMO or a LUMO that could serve for a "through-space" type of transfer in these systems.

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