$F{\equiv}CTF$, the T-for-H substitution products, stays constant with moderation either in the presence or the absence of O_2. This implies that $CT{\equiv}CF$ is also formed by primary recoil tritium substitution reactions as shown in eq 5 and 21 and that these T-for-H and T-for-F substitutions have similar energy dependence. On the other hand, the increase in the $CH{\equiv}CT$ yield with He moderation parallels those of $CHT{=}CF_2$ and $CHT{=}CHF$, indicating the similarity in their formation mechanism. Such common behavior lends support to the notion that $CH{\equiv}CT$ is formed via the excited bridged complex, as discussed earlier in this section.

However, certain features about these two less important products are not easily explainable. For example, it is difficult to account for their rather high yields in the recoil tritium reaction with $CHF{=}CHF$ systems. In the corresponding $CH_2{=}CF_2$ system, their yields relative to the T-for-H substitution product are at least a factor of three to five less.

The HT Yield. The HT to $CHF{=}CTF$ ratios from both *cis*- and *trans*-$CHF{=}CHF$ systems are both around 0.3, in comparison with a HT/C_2H_3T ratio of 0.23 from recoil tritium reactions with C_2H_4[10] and a HT/CH_3T ratio of 0.79 from the corresponding CH_4 system.[31] The rather low HT yield implies that the $D(C{-}H)$ values in $CHF{=}CHF$ are likely to be well above 100 kcal mol^{-1}.

The results also show that the HT yield decreases with the addition of O_2 as a scavenger and increases sharply with He moderation. Both of these observations are consistent with the notion that H abstraction by recoil tritium atoms is a rather low energy process.[1-3]

Conclusion

Among other features, the two main conclusions of this work on recoil tritium reactions with *cis*- and *trans*-$CHF{=}CHF$ are as follows: (i) the tritium-labeled parent compound is formed mainly from the direct T-for-H substitution process while the geometric isomer is formed via unimolecular isomerization of the excited tritium-labeled parent compounds; (ii) the recoil tritium addition process will give rise to an excited radical, which immediately converts into a bridged complex. Such a bridged complex may isomerize to effect a net 1,2 F-atom migration to give $CHT{=}CF_2$ as the final product. It can also either expel an F atom to form $CHT{=}CHF$ or undergo further decomposition to give $CH{\equiv}CT$ through HF elimination.

Acknowledgment. This work is kindly supported by the Robert A. Welch Foundation. The technical help of Deborah L. Morris is also appreciated.

Registry No. *cis*-$CHF{=}CHF$, 1630-77-9; *trans*-$CHF{=}CHF$, 1630-78-0; tritium, 10028-17-8.

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Resonance Raman Spectra and Electronic Structure of the μ-Disulfur-Bridged Diruthenium Complex $[(H_3N)_5RuSSRu(NH_3)_5]^{4+}$ and Related Systems[1]

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Abstract: The resonance Raman spectra of the μ-disulfur-bridged complex $[(H_3N)_5RuSSRu(NH_3)_5]^{4+}$, **1**, has been determined. An excitation profile reveals that the intense, totally symmetric Ru–S stretching vibration, which is the dominant feature of these spectra, is coupled to a single, intense, low-energy electronic transition (λ 715 mm, ϵ 14990) involving electrons delocalized over the Ru–S–S–Ru core. These observations establish that the Ru–S–S–Ru unit in this and certain related complexes is an electronically unique, independent chromophore. The suggested assignment for this transition, based on a qualitative molecular orbital description of the π-bonding in **1**, involves the promotion of an electron from a π-antibonding b_g orbital to a π-antibonding a_u orbital. It further follows that the only reasonable formulation of the electronic configuration in this molecule is Ru(III)–S–S–Ru(III). The utility of these observations, concepts, and conclusions as they relate to the electronic structure of other μ-dichalcogenide-bridged complexes is discussed.

Early studies of μ-dichalcogenide-bridged transition metal complexes concentrated on peroxo- and superoxo-bridged species with the aim of establishing categories of geometry and bonding.[2a,b] In turn, these investigations have provided insights about the nature of dioxygen-transition metal coordination.

More recently, attention has begun to focus on μ-dichalcogenide-bridged complexes in general, i.e., compounds which, as a class, are characterized by a M–X–X–M (X = S, Se, Te) linkage. Among the earliest characterizations of such complexes are those of Taube and co-workers,[3] who prepared the complex tetrabromo-μ-disulfurdecaaminodiruthenium, $[(H_3N)_5RuSSRu(NH_3)_5]Br_4$, **1**, along with a series of related homologues, $[(L)(H_3N)_4RuSSRu(NH_3)_4(L)]^{n+}$, and those of Siebert and Thym,[4] who reported the synthesis and partial characterization of hexapotassium μ-disulfurdecacyanodicobalt(III), $K_6[(NC)_5CoSSCo(CN)_5]$, and hexapotassium μ-diseleniumdecacyanodicobalt(III), $K_6[(NC)_5CoSeSeCo(CN)_5]$. Following these and subsequent studies,[5-7] the initial novelty of μ-dichalcogenide-

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[†] Rutgers University.
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[1] This research was supported by DOE contract DE-AS05-80ER-1062 and NSF Grant 80-17405.

[2] (a) Cf. Lever, A. B. P.; Gray, H. B. *Accounts Chem. Res.* **1978**, *11*, 348, and references therein. (b) Martin, R. L. "New Pathways in Inorganic Chemistry"; Cambridge University Press, 1968. (c) DiSalvo, F. J.; Waszczak, J. V. *Phys. Rev.* **1981**, *B23*, 457. (d) Mononuclear ruthenium species serve as precursors to **1**; also compound **1** undergoes spontaneous decomposition in solution to a complex mixture of uncharacterized ruthenium-containing products.

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[4] Siebert, H.; Thym, S. *Z. Anorg. Allg. Chem.* **1973**, *399*, 107.

[5] For a review of earlier as well as subsequent papers, see: Kuehn, C. G.; Isied, S. S. *Prog. Inorg. Chem.* **1979**, *27*, 153.

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bridged complexes has been gradually replaced by a recognition that, as a structural unit, such complexes are proving more common than heretofore anticipated. Moreover, beyond their intrinsic interest, the transition metal complexes of sulfur and disulfur have received considerable current attention because of the increased insight they portend for our understanding of the function of several important enzymes and proteins.[5]

In discussing **1**, Tabue and co-workers suggested two alternative formulations, viz., that **1** could be viewed as involving (a) two ruthenium(III) centers bridged by a common disulfide ligand, S_2^{2-}, or (b) as two ruthenium(II) centers bridged by a singlet disulfur. In a subsequent single-crystal X-ray crystallographic investigation, Elder and Trkula[8] considered these proposals along with a third alternative formulation involving a "supersulfide" ligand, $S_2^{-}\cdot$, bridging a Ru(III) center and a Ru(II) center. These same authors concluded that it is this latter formulation which provides the major contribution to, and therefore most resonable descritpion of, the electronic structure of the Ru–S–S–Ru core in **1**.

We report here the results of our investigation which suggests that the physical and spectroscopic properties of **1**, along with those of certain related complexes, are more accurately described by an electronic structure in which the Ru–S–S–Ru core (and quite probably the M–X–X–M core in selected homologues) is formulated as an electronically unique and independent chromophore, a reasonable bonding description of which is provided by a qualitative orbital treatment employing the atomic orbitals of ruthenium(III) and the molecular orbitals of S_2^{2-} as a basis set.

Results and Discussion

Magnetism. The magnetic susceptibility of $[(NH_3)_5RuSSRu(NH_3)_5]Br_4$ was measured from 300 to 4.2 K using a Faraday balance.[2c] The susceptibility followed the simple Curie Weiss form and a least-squares fit gave the following parameters: $\chi_g = 4.296 \times 10^{-5}/(T + 0.2) - 0.282 \times 10^{-6}$ emu/g. An effective magnetic moment of 0.52 μB per Ru pair is calculated from the Curie constant. Such a low moment could only arise from a state with a low g value, a situation not unlikely in Ru, since Ru has a large spin–orbit coupling.

In order to search for this state, the ESR spectrum of the solid compound was measured in a wideline spectrometer (at 9.26 GHz). At room temperature a broad resonance centered near $g \approx 3.6$ (1830 g) was observed. This resonance shifted and sharpended into a two-peak spectrum at low temperatures (5 K) with g values near 2.5. The concentration of spins was estimated to be 10^{17} (within a factor of 5) for the 100-mg sample. These large g values are inconsistent with the interpretation of the magnetic susceptibility being due to a moment on each Ru pair, since the g value would have to be less than 0.7 (if $n_{\mathrm{eff}} = g[S(S + 1)]^{1/2}$ μB and $S = {}^1/_2$). We attribute this behavior to the presence of a small amount (~1%) of a second cmpound, such as an Ru(III) and/or Ru(IV) monomer.[2d] We conclude that the magnetic moment observed here and previously[3] is due to an impurity in which case **1** is diamagnetic with $\chi_g = -0.282 \times 10^{-6}$ emu/g.

Vibrational Assignments. In their original investigation, Taube and co-workers[3] reported that the Raman spectrum of **1**, determined as an aqueous solution using 488.0-nm exciting radiation, exhibited a band of 519 ± 2 cm^{-1}. A band of similar position was also observed for the related ions $[L(H_3N)_4RuSSRu(NH_3)_4L]^{n+1}$, L = H_2O, Cl^-, isonicotinamide. Based on the fact that the S–S stretching frequency observed for a great many μ-disulfides, including H_2S_2, R_2S_2, and X_2S_2 (X = halogen), occurs within the frequency range 522 ± 27 cm^{-1},[9] the 519-cm^{-1} band in **1** was assigned as ν (S–S).

Figure 1A shows the Raman spectrum of solid **1** determined with 488.0-nm incident radiation. Here, too, the band at 519 cm^{-1} is readily apparent and its assignment as ν(S–S) remains no less reasonable. However, as Figure 1 reveals, the Raman spectrum of **1** also exhibits a strong dependence on the frequency of the incident radiation. Indeed, as this frequency approaches the maximum of the intense, low-energy electronic absorption that uniquely characterizes this family of complexes (vide infra), the resulting Raman spectra are increasingly dominated by a single, intense band centered at 415 ± 2 cm^{-1} together with overtone bands at 824, 1236, and 1648 cm^{-1}. Such behavior, of course, is characteristic of substances in which a strong resonance Raman effect is operative. Additional confirmation of this line of reasoning is seen in the excitation profile for the 415-cm^{-1} band (Figure 2), where the intensity of this mode is seen to closely track that of the band centered at 715 nm (ϵ 14 990). We conclude, therefore, that the 415-cm^{-1} band is coupled to this electronic transition. Moreover, with a depolarization ratio of $\rho_1 \approx 0.35$, it follows that this vibration represents a totally symmetric (A_1) mode and that as such, is coupled to only the 715-nm absorption.[10]

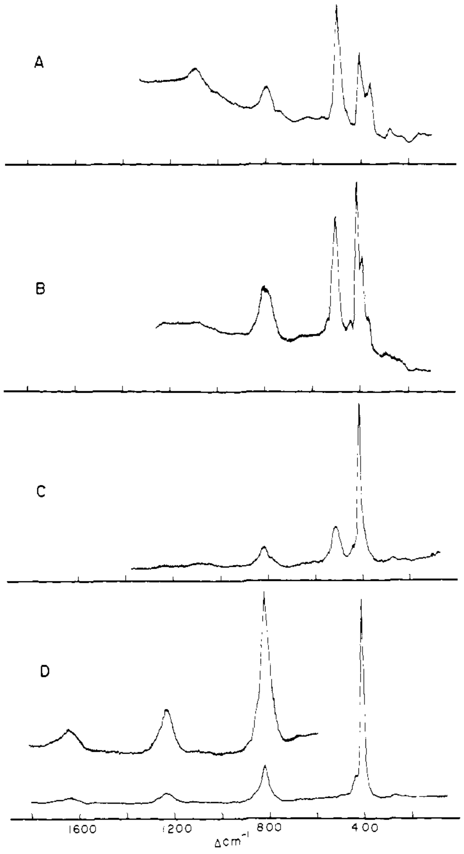
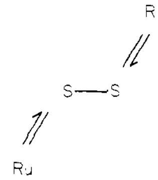


Figure 1. A comparison of the solid-state Raman spectra of $[(H_3N)_5RuSSRu(NH_3)_5]Br_4$ recorded with an excitation frequency of (A) 488.0 nm; (B) 530.9 nm; (C) 568.2 nm; and (D) 647.1 nm.

We assign the 415-cm^{-1} vibration as ν(Ru–S) based upon the range observed for a variety of metal–sulfur stretching frequencies (485–210 cm^{-1})[11] and the consistency which this assignments lends to the interpretation of the low-energy electronic spectrum of **1** (vide infra). Furthermore, in view of symmetry restrictions, it can be additionally concluded that the 415-cm^{-1} band corresponds to a simultaneous stretching of *both* Ru–S bonds, i.e.



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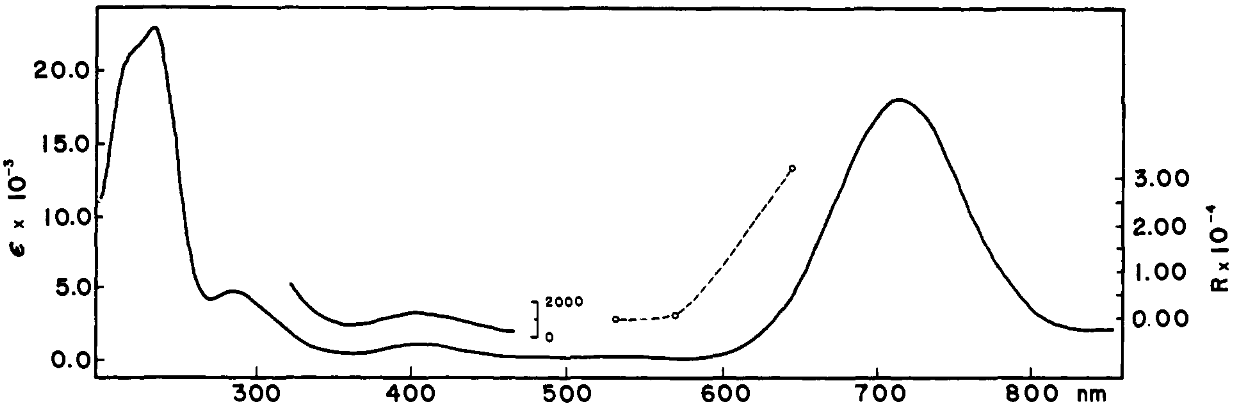

Figure 2. A comparison of the visible absorption spectrum of $[(H_3N)_5RuSSRu(NH_3)_5]^{4+}$ ion and the relative intensities (O) of the Ru–S stretching vibration. Both Raman and absorption spectra were recorded in 1 M HCl solution. R_{mol} is the molar intensity of the 1048-cm^{-1} (ν_1) band of KNO_3 added as an internal standard. All integrated intensities are corrected for photomultiplier tube response. The three excitation frequencies employed are 530.9, 568.2, and 647.1 nm.

It follows that these vibrations must accompany a significant and equivalent change in the Ru–S orbitals leading to the conclusion that the Ru–S–S–Ru core is acting as a chromophoric group.

MO Description. The above considerations concerning the nature of the Ru–S–S–Ru linkage in **1** suggest that molecular orbital theory may provide a meaningful description of the bonding in this and related systems. We have constructed a qualitative molecular orbital description of **1** and find that it does, indeed, readily explain the distinctive properties of this ion. In so doing we assumed that, as with any chromophoric grouping, the electrons responsible for the characteristic absorption are localized on the constituent atoms, in this instance the four-atom Ru–S–S–Ru grouping which, in the solid state shows a dihedral angle of 180°, and thus, has a trans planar geometry.[8] Now, if the plane of the Ru–S–S–Ru unit is assigned as the *yz* plane of a Cartesian coordinate system and the further assumption made that the ligand field around each Ru(III) ion is essentially octahedral, then the local symmetry at each Ru atom can be treated as C_{2v}.[12] Under these circumstances the relevant orbitals transform as $A_1(s, p_z, d_{x^2-y^2}, d_{z^2})$, $A_2(d_{xy})$, $B_1(d_{xz}, p_x)$ and $B_2(d_{yz}, p_y)$ or a summed representation of $4A_1 + A_2 + 2B_1 + 2B_2$ for each Ru center. The set of five (5) σ bonds formed by the ammonia ligands transform as $2A_1 + A_2 + B_1 + B_2$ while the Ru–S σ bond transforms as A_1. The five electrons on each Ru center must, therefore, be assigned to the remaining metal orbitals which transform as A_1, B_1, and B_2. These localized orbitals, in turn, yield a set of six (6) molecular orbitals which conform to the C_{2h} symmetry of the entire molecule: a_g, b_g, a_g, b_u, a_u, and b_u.

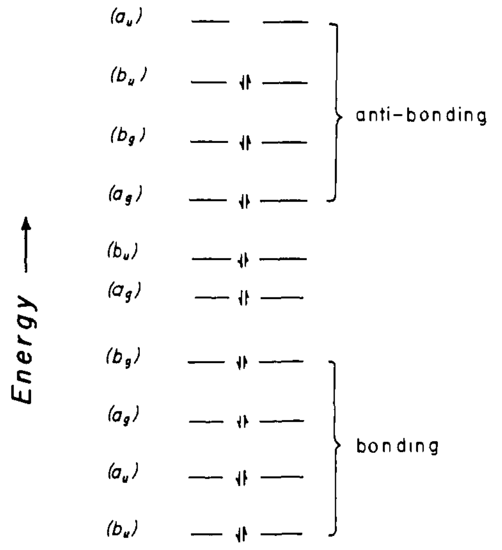

Figure 3. Diagram showing the relative energies expected for the π component of the molecular orbital scheme for $[(H_3N)_5RuSSRu(NH_3)_5]^{4+}$. The energy ordering is determined from the nodal patterns and expectations concerning the splitting of the d and p orbitals in a C_{2h} ligand field.

Turning to the electronic nature of the disulfide bridge, we note that previous studies have established the electronic structure of R–S–S–R (R = H, CH_3) and, moreover, reveal its strong dependence on the R–S–S–R dihedral angle.[13] Thus, for a molecule having the C_{2h} symmetry of the Ru–S–S–Ru moiety, the following *π components* are available: b_g, a_g, a_u, and b_u. Assuming a similar electronic structure is maintained for the disulfide linkage in $[L_5Ru–S–S–RuL_5]^{4+}$, it follows that the out-of-plane antibonding orbital, b_g, the out-of-plane π-bonding orbital, a_u, the in-plane antibonding a_g orbital, and the in-plane π-bonding orbital b_u, have the correct symmetry to combine with, respectively, the b_g, a_u, a_g, and b_u orbitals on each ruthenium center. This linear combination results in the formation of four nondegenerate π-bonding orbitals, b_g^b, a_g^b, a_u^b, and b_u^b, and four nondegenerate π-antibonding (π^*) orbitals. If the remaining orbitals, i.e., a_g and b_u are assigned nonbonding status, then the resulting ground state configuration (exclusive of σ components) for $[(H_3N)_5RuSSRu(NH_3)_5]^{4+}$ is given by

$$(b_u^b)^2(a_u^b)^2(a_g)^2(b_g)^2[(b_u)^2(a_g)^2](a_g^a)^2(b_g^a)^2(b_u^a)^2(a_u^a)^0$$

where the orbitals in the square brackets are approximately degenerate. A diagram showing the relative energies of the molecular orbital scheme for $[(H_3N)_5RuSSRu(NH_3)_5]^{4+}$ is shown in Figure 3. Filling these orbitals with the available valence electrons (5 from each ruthenium and 8 from the disulfide unit) results in an electronic structure which readily explains the apparent physical and spectral properties of this molecule. Thus, the effective diamagnetism of **1** is a clear consequence of the pairing of odd electrons made possible by a mechanism of π bonding. Also, the apparent reduction in both the Ru–S and the S–S bond lengths from those anticipated from the sum of single-bond radii[8] becomes a natural consequence of the π character which such bonding introduces. This latter consequence is presumably also responsible for the enhanced kinetic lability of the *trans* ammine ligand. Moreover, the *trans* planar geometry of the Ru–S–S–Ru unit is a direct consequence of π bonding: any departure from it would diminish the degree of π-bonding and hence molecular stability.

Finally, the molecular orbital treatment presented here explains the otherwise inexplicably intense, low-energy absorption in the visible spectrum of the $[(H_3N)_5RuSSRu(NH_3)_5]^{4+}$ ion. Thus, the likeliest transitions in the present molecular orbital framework

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(12) The local symmetry of each Ru center is clearly C_4; however, it is no less correct—and for the purposes of the present discussion more convenient—to assign the local symmetry as belonging to two subgroups of the O_h point group, viz., C_{2v} and C_v, the latter element corresponding to a *yz* plane of symmetry; see: Ross, S. D. "Inorganic Infrared and Raman Spectra"; McGraw-Hill: New York, 1973.

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are: $b_u^a \rightarrow a_u^a$, $b_g^a \rightarrow a_u^a$, $a_g^a \rightarrow a_u^a$, $a_g^{nb} \rightarrow a_u^a$, $b_u^{nb} \rightarrow a_u^a$, $b_g^b \rightarrow a_u^a$, $a_g^b \rightarrow a_u^a$, $a_u^b \rightarrow a_u^a$, and $b_u^b \rightarrow a_u^a$. Four of these proposed transitions ($b_u^a \rightarrow a_u^a$, $b_u^{nb} \rightarrow a_u^a$, $a_u^b \rightarrow a_u^a$, and $b_u^b \rightarrow a_u^a$) can be immediately dismissed because they involve electric-dipole-forbidden processes. Of the remaining five possibilities, only one, $b_g^a \rightarrow a_u^a$, is expected to have any appreciable intensity. This statement follows from a consideration of the magnitude of the transition dipole moment, μ, in the approximate expansion of the relevant MO is terms of the atomic orbitals localized of Ru(1), Ru(2) and the appropriate molecular orbitals of S_2. Thus

$$\begin{aligned}\mu_{b_g^a \rightarrow a_u^a} = {} & \langle d_{xz}(M_1)|\mu|d_{xz}(M_1)\rangle - \langle d_{xz}(M_2)|\mu|d_{xz}(M_2)\rangle - \\ & (d_{xz}(M_1)|\mu|a_u(S_2)\rangle + \langle d_{xz}(M_2)|\mu|a_u(S_2)\rangle + \\ & \langle b_g(S_2)|\mu|a_u(S_2)\rangle - (b_g(S_2)|\mu|d_{xz}(M_1)\rangle - \\ & \langle b_g(S_2)|\mu|d_{xz}(M_2)\rangle = -2\langle d_{xz}(M)|\mu|a_u(S_2)\rangle\end{aligned}$$

which reduces to $\mu_{b_g^a \rightarrow a_u^a} = -2R_{\text{M-S}}$, where $R_{\text{M-S}}$ is the length of the metal–sulfur bond. However, at the same level of approximation, the remaining transitions show a transition dipole moment with a magnitude of ca. zero. We conclude, therefore, that only the $b_g^a \rightarrow a_u^a$ transition can be expected to have an appreciable intensity. Moreover, it can be shown by local symmetry arguments that this transition will have z polarization.[14]

The above facts explain nicely why ν(Ru–S) is significantly enhanced while the ν(S–S) is not. Thus, within the stated molecular orbital frame work, the only transition dipole moment of any significant magnitude lies along the Ru–S bond, i.e., the z axis. Since the S–S bond lies significantly off this axis, the S–S stretching frequency can *not* experience a comparable intensity enhancement. It further follows that the Ru–S–S–Ru chromophore is *not* accurately described as a mixed valence Ru(II)–Ru(III) system, since this arrangement would require a dipole moment that operates along the S–S bond with the clear requirement that both ν(Ru–S) and ν(S–S) must be similarly enhanced. Therefore, we conclude that the totally symmetric Ru–S stretching vibration in $[(H_3N)_5RuSSRu(NH_3)_5]^{4+}$ is in resonance with an electronic transition which, within the framework of the MO description presented here, corresponds to the promotion of an electron from a filled π-antibonding to an unfilled π-antibonding orbital. As the b_g orbital is recognized as having substantial ligand character while the a_u^a orbital is seen to possess largely metal character, such a transition would be viewed from a ligand-field (LF) perspective as a ligand-to-metal charge transfer (LMCT). Moreover, since this transition is z-polarized,[14] it follows that α'_{zz} is the dominant element in the Raman scattering tensor that is enhanced by resonance.

It is reasonable to consider the extension of the molecular orbital description illustrated in Figure 3 to the corresponding selenium homologues, viz., $[(H_3N)_5RuSeSeRu(NH_3)_5]^{4+}$. Indeed, this complex has recently been observed[6] and its electronic spectrum paralles that of $[(H_3N)_5RuSSRu(NH_3)_5]^{4+}$. Specifically, the intense, low-energy absorption which uniquely characterizes the visible spectrum of the μ-disulfide is also observed, correspondingly red-shifted: $\lambda_{\max}$ 830 nm, ϵ 1.4 × 10^4.

In light of the above molecular orbital description, it follows that the corresponding complex of Ru(II), i.e., $[(H_3N)_5RuXXRu(NH_3)_5]^{2+}$, being a closed-shell structure, would not be expected to exhibit the intense, low-energy transition in its visible spectrum that characterizes the Ru(III) complexes. Unfortunately, such Ru(II) complexes are not known; however, similar μ-disulfide and μ-diselenide complexes of the isoelectronic ion Co(III) are known. Specifically, Sievert and Thym[4] have reported the preparation and characterization of $[(NC)_5CoSSCo(CN)_5]^{6-}$ and $[(NC)_5CoSeSeCo(CN)_5]^{6-}$. Consistent with this expectation, we found that the electronic spectra of these ions exhibited no significant ($\epsilon > 10^3$) absorption at $\lambda > 500$ nm. Likewise, in our hands the Raman spectra of these complexes exhibited only a relatively weak, low-frequency band tentatively attributable ν(Co–X). The geometrical disposition of the Co–X–X–Co unit in these systems is not known and their structural characterization would clearly be desirable in extending our understanding of such systems and their relationship to that of **1**.

Concluding Remarks. A variety of coordination geometries are known for μ-disulfur–metal complexes.[5,15] None, however, share the simplicity of composition and structure of **1** and its related species. Still, the strong similarities between the physical and spectral properties of **1** and several of these more complicated complexes suggest the possibility that the nature of the bonding within these M–S–S–M cores may be partially related. Thus, for example, the complex $[(\eta\text{-}C_5H_5)_2Fe_2(S_2)(SC_2H_5)_2]$, **2**, formally a complex of Fe(III), is diamagnetic and exhibits an electronic spectrum similar to that of **1**. In particular, both **1** and **2** exhibit an intense, low-energy transition (715 and 840 nm, respectively). Kubas and Vergamini have suggested the possiblity that the 840-nm band in **2** originates in a disulfur → metal charge transfer.[16] Such an assignment is consistent with the qualitative molecular orbital description they proposed and also concurs with our assignment of the 714-nm band in **1**.

Previous descriptions of the electronic nature of **1** deserve brief comment. These formulations have relied heavily on valence bond descriptions.[8] The general inadequacies of such descriptions in describing the core-bonding in dioxygen–metal complexes is now widely recognized.[2a] If anything, these failings are only magnified in disulfur–metal complexes.

Finally, it is interesting to note the similarities that exist between the bonding and electronic behavior in the RuSSRu chromophore and those reported previously for the Ru–O–Ru, Os–O–Os, and W–O–W chromophores in a series of closely related, linear μ-oxo-bridged complexes.[10] Moreover, it is attractive to contemplate to what extent the conclusions described above for **1** can be extended to other dichalcogenide–metal complexes and especially to describing the nature of the bonding in certian biologically relevant model systems.[5,15]

Experimental Section

Crystalline samples of $[(H_3N)_5RuSSRu(NH_3)_5]Br_4$ were prepared as described by Taube and co-workers.[3] The μ-disulfur and μ-diselenium complexes of cobalt, $K_6[(NC)_5CoSSCo(CN)_5]\cdot 4H_2O$ and $K_6[(NC)_5CoSeSeCo(CN)_5]\cdot 5H_2O$, were synthesized according to the procedures reported by Siebert and Thym.[4]

Raman spectra were determined on a Cary Model 82 spectrometer equipped with a triple monochromator and a krypton and an argon (Coherent Model 52) ion laser. Ultraviolet and visible spectra were determined on a Cary Model 17D spectrophotometer.

Solution Raman spectra were determined on freshly prepared, dilute samples in concentrations ranging from 2 × 10^{-4} to 5 × 10^{-3} M. Spectra were determined using a rotating cell.[17a] Raman intensities were determined by adding a known amount of internal standard to the solution and comparing the intensity of the band of interest to that of the $\nu_1(A_1)$ line of the internal standard. At least three spectral scans were made for each determination and the peak areas were measured directly with a polar planimeter. The resulting intensity ratios were averaged, converted to a molar basis, and corrected for phototube response.

Solid-state Raman spectra were obtained with the aid of a rotating cell.[17b] Intensities were determined by adding a known amount of an internal standard such as KNO_3 to the desired complex and homogenizing the mixture in a Spex Wig-L-Bug. Integration and normalization procedures were the same as those described for solution samples.

Acknowledgment. We thank R. S. Hutton for performing the EPR measurements and F. J. DiSalvo for discussions concerning the magnetic and EPR measurements.

Registry No. $[(H_3N)_5RuSSRu(NH_3)_5]Br_4$, 42720-73-0.

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[14] The molecular symmetry of the Ru-S-S-Ru core is C_{2h}. In this point group the totally symmetric (A_{1g}) vibrations have scattering tensors with diagonal elements only, i.e., α'_{xx}, α'_{yy}, and α'_{zz}. Under such circumstances the depolarization ratio can be shown to reduced $\rho_1 \simeq {}^1/_3$ (cf. Hester, R. E. "Raman Spectroscopy", symanski, H. A., Ed.; Plenum Press: New York, 1967; Chapter 4.

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