high specificity for the ligand. Receptor **2**, with $K_a = 8 \times 10^6$ M^{-1} for TNS, efficiently moves a small organic ligand (TNS or BNS) from the vesicle surface to the interior of the extended cavity provided by the bis-CD. The location of the resulting complex is still unclear, though it seems likely that the complex adsorbs to the vesicle surface in view of the relatively hydrophobic nature of portions of the exterior surface of β-CD. If so, then **1**, **2**, and **3** constitute the first synthetic membrane-bound receptors for organic ligands.

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"Molecular Hysteresis"

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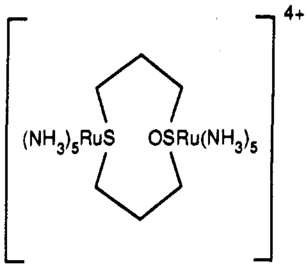
An early example of linkage isomerization coupled to electron transfer[1] is the redox behavior of the $[(NH_3)_5Ru(\text{dimethyl sulfoxide})]^{3+/2+}$ couple. When the S-bound isomer, $[(NH_3)_5Ru(SO(CH_3)_2)]^{2+}$, is oxidized by cyclic voltammetry, this change occurs at ca. 1.0 V vs NHE. The Ru–S linkage is retained in the immediate product of the reaction, but this then rearranges to the more stable O-bound form (specific rate at room temperature, 7.0×10^{-2} s^{-1}). To reduce the rearranged product, a potential more negative by almost 1 V than that required for oxidation of the S-bound form of Ru(II) must be applied, and the immediate product of the reduction is $[(NH_3)_5Ru(OS(CH_3)_2)]^{2+}$, which then rearranges to the more stable original state ($k = 30 \pm 7$ s^{-1}).

In the molecule we have synthesized, a reversible couple is combined with that just described so that there is the possibility of communication between the metal centers in the binuclear species. The reversible couple was chosen to have a potential bracketed by the irreversible potentials of the sulfoxide couple. We prepared (1,5-dithiacyclooctane 1-oxide)bis(pentaammineruthenium(II)) by the reaction of $[Ru(NH_3)_5(OH_2)]^{2+}$ with the bridging ligand[2] in acetone.



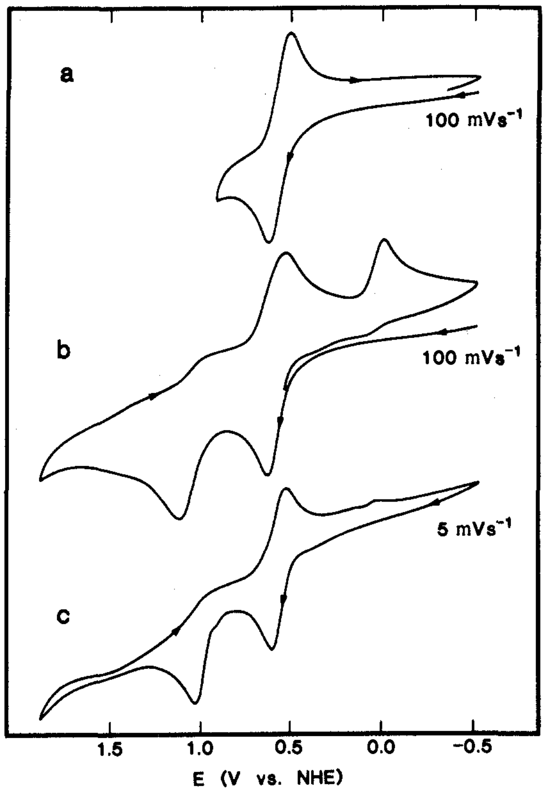


Figure 1. Cyclic voltammograms of the binuclear species as a function of scan rate.

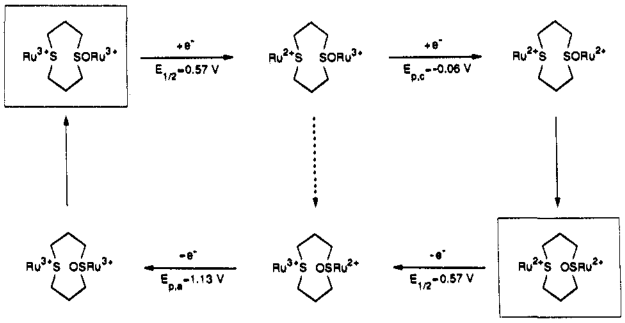


Figure 2. Hysteresis loop in the electrochemistry of the binuclear species. The specific rates for the linkage isomerization reactions reading from left to right (s^{-1}): $(5 \pm 0.5) \times 10$, $<4 \times 10^{-2}$, $(2.0 \pm 0.2) \times 10$, respectively.

The behavior of this redox system in cyclic voltammetry[4] is shown in Figure 1. On scanning to an oxidation potential short of that required to oxidize the Ru(II)–sulfoxide center, a reversible couple ($E_{1/2} = 0.57$ V) appears (Figure 1a), which is close to that observed for other $[\text{pentaammineruthenium}]^{3+/2+}$ couples in which the heteroligand is a thioether.[5] Figure 1b shows the electrochemical behavior when the oxidation scan (100 mV s^{-1}) is continued to potentials high enough to involve also the sulfoxide center. As new features, we now observe an oxidation wave at 1.13 V, without a corresponding reduction wave, and reduction at −0.06 V, without a corresponding oxidation wave, these features being very much like those that would be expected for the mononuclear sulfoxide complex at sufficiently slow scan rates. The electrochemical behavior of the binuclear system can be represented by the scheme shown in Figure 2, but where the kinetic parameters are yet to be entered. It is to be noted that two states of the mixed-valence species are produced. One of the states is accessible only by reduction of the stable form $[S^{3+}/(OS)^{3+}]$, and the other, only by oxidation of the stable form $[S^{2+}/(SO)^{2+}]$. Starting with either of the stable extreme states, the loop made by following in the direction of the solid arrows has important features in common with the familiar hysteresis loop exhibited by certain ferromagnetic materials.

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(1) Yeh, A.; Scott, N.; Taube, H. *Inorg. Chem.* **1982**, *21*, 2542.

(2) The ligand was prepared from 1,5-dithiacyclooctane, by the method of Roush and Musker: Roush, P. B.; Musker, W. K. *J. Org. Chem.* **1978**, *43*, 4295.

(3) All manipulations were done under dry argon in a Vacuum Atmospheres Co. glovebox. ^1H NMR (acetone-d_6, PF_6 salt): δ 2.0–2.1 (m, 4 H), 2.7–2.9 (m, 4 H), 3.8–3.9 (m, 4 H), 2.47 (s, 12 H), 2.55 (s, 12 H), 3.33 (s, 3 H), 3.81 (s, 3 H). The compound was isolated as a PF_6 salt with one acetone. Anal. Calcd for $C_9H_{48}N_{10}O_2S_2P_4F_{24}Ru_2$: C, 9.20; H, 4.11; N, 11.92. Found: C, 8.96; H, 4.08; N, 11.24.

(4) All voltammograms were measured in a standard three-electrode cell and are reported vs the normal hydrogen electrode. The reference electrode was calibrated with the ferrocene/ferrocenium couple ($E = 0.55$ V (NHE)) as measured in situ.

(5) Stein, C. Ph.D. Thesis, Stanford University, 1978.

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At scan rates above 10 V s^{-1}, the waves complementary to those for oxidation at 1.1 V, and the reduction at −0.06 V, appear. By application of the method of Nicholson and Shain,[6] the specific rates for the S to O isomerization of the metastable 3+ species and the O to S isomerization of the metastable reduced species were determined as $(5.0 \pm 0.5) \times 10$ s^{-1} and $(2.0 \pm 0.2) \times 10$ s^{-1}, respectively. At low scan rates, <20 mV s^{-1}, the reduction wave at $E_{pc} = -0.06$ V decreases in amplitude, as is seen by comparing Figure 1c with Figure 1b. Intramolecular electron transfer can cause such a decrease, but other processes, for example, intermolecular electron transfer and loss of the electroactive species from the diffusion layer, can also contribute, so that, in the absence[7] of a more complete study, we can only set the upper limit, 4.1×10^{-2} s^{-1}, on the rate of intramolecular electron transfer.

The intervalence band for the stable form of the mixed-valence species, $[S^{3+}/(SO)^{2+}]$, measured in acetone, has a maximum at ~640 nm with $\epsilon \sim 4 \times 10$ M^{-1} cm^{-1}. The shift to high energies, as compared to substitutionally symmetric species, is a reflection of the difference in the redox potentials for the two sites. There is a second much stronger absorption at 452 nm which we attribute to ligand to metal charge transfer at Ru(III).[8]

The more usual redox couples conform to the Marcus relationship,[9] a necessary condition for its validity being that the distortions that bring energy matching at the two sites are nearly harmonic. Those in which the potential profile for at least one oxidation state has two minima—in our case, this is true in both oxidation states—comprise an important class which has not been investigated systematically. Devices of the kind we have described provide a means of studying electron transfer for them in the intramolecular mode. They may also provide a means of locking in charge transfer brought about by light absorption and, as such, may find application in high-density storage of memory. The excited state $[S^{2+}/(SO)^{3+}]^*$ which arises on absorption of light at ~640 nm is expected to be quenched rapidly, and if intramolecular electron transfer is slow enough, isomerization to $[S^{2+}/(OS)^{3+}]$ will occur.

Many examples of geometrical isomerization accompanying a change in oxidation states have been reported,[10] particularly by Bond and co-workers.[11] The appearance of linkage isomerizations, which depends on a change in back-bonding capacity attending a change in oxidation state, is predictable for many yet untested systems with a reasonable degree of certainty. The field has been greatly extended in the study of molecules in which the metal ion is bound by η^2 to organic ligands,[12] including aromatic molecules, and additional chromophores can easily be built into mixed-valence molecules. It needs to be acknowledged that there is precedent for the "double square" potential diagram featured in Figure 2.[13] The system that we describe is to be regarded as a prototype of others which can be devised to show "molecular hysteresis" and to our knowledge is the first to be deliberately synthesized to exhibit this behavior.

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(6) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

(7) Work on this system was interrupted by Sano's return to Nagoya University and will be continued there.

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(10) Copious reference to earlier literature is made in the following: Gaudiello, J. G.; Wright, T. C.; Jones, R. A.; Bard, A. J. *J. Am. Chem. Soc.* **1985**, *107*, 888.

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Preparation and Characterization of Layered Lead Halide Compounds†

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Recent reports of a very strongly bound exciton in the excited state of the layered perovskite-type compounds $(RNH_3)_2PbI_4$ (R = nonyl, decyl, ...)[1,2] renewed our interest in lead halide compounds, since significant third-order optical nonlinearity is often associated with such exciton-exhibiting materials.[3] During studies of the chemistry and optical properties of this and related compounds, we have discovered a novel series of layered lead halo compounds having related excited-state features, some of which are described herein.

Evaporating acetone, tetrahydrofuran (THF), or dimethylformamide (DMF) solutions of PbI_2 and RNH_3I (R = nonyl, decyl) provided thin films[4] of the reported compounds $(RNH_3)_2PbI_4$ having a strong, sharp absorption feature at 511 nm, consistent with the value of 2.44 ev (508 nm) reported for the exciton transition.[1] Pump–probe experiments[5] at ambient temperature showed that the exciton transition in films[4] of the decylammonium compound can be bleached efficiently, which means there exists a large resonant third-order optical nonlinearity. In the low-power regime, the bleaching efficiency, expressed as $\Delta a/Ia_0$ where a_0 is the ground-state absorption coefficient, Δa is the laser-induced absorption change, and I is the laser intensity, is 1.5×10^{-7} cm^2/W at 510 nm. This is a relatively large value but somewhat less than that observed for small CdS clusters.[5] Transient absorption limits the maximal bleachable exciton absorption to ~27%.[6]

We hoped to find closely related compounds that retain the sharp "exciton" absorption feature but shifted to significantly lower energies. Incremental changes in chain length of the alkylammonium cation have little effect on the room temperature absorption feature of orange-colored $(RNH_3)_2PbI_4$.[1] However, use of methylammonium cation provides the very darkly colored compound $(MeNH_3)PbI_3$ in the cubic perovskite phase[7,8] (see Figure 1a), and we began to suspect that the cubic perovskite $(MeNH_3)PbI_3$ and the layered perovskite $(RNH_3)_2PbI_4$ (Figure 1b) are actually two extremes of a hitherto unknown structural series $(RNH_3)_2(MeNH_3)_{n-1}Pb_nI_{3n+1}$ (Figure 1). Here $n = \infty$ corresponds to the cubic perovskite compound $(MeNH_3)PbI_3$[7] (Figure 1a) and $n = 2, 3, \ldots$ ("bilayer", Figure 1c, "trilayer", ...) describe structures not previously known for any organic amine–metal halide systems.[9]

[†] Contribution No. 5582.

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