dium(V) in the last step of Scheme V takes place. A reaction between two radicals (*e.g.*, disproportionation) would offer a plausible explanation.

Our results thus rule out Scheme I for the chromic acid oxidation of cyclobutanol. Furthermore, preliminary experiments[8] *show that isopropyl alcohol and a number of primary alcohols as well as aldehydes exhibit similar behavior, making it unlikely that Scheme I is correct for any alcohol or related compound.*

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(8) M. Rahman and J. Roček, unpublished results.

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A New Type of Intramolecular Antiferromagnetism[1]

Sir:

The lanthanide metals are thought to consist of magnetic ion cores surrounded by conduction electrons derived from 6s and 5d orbitals. The ferro- and antiferromagnetic magnetic properties of these substances are attributed to the interion coupling of the metal ion core 4f electrons *via* conduction electron polarization which results from direct exchange interaction of the 4f electrons and the 6s and 5d conduction electrons.[2]

We wish to report evidence for a new type of intramolecular antiferromagnetism in a formally low-valent complex of europium with bipyridyl and suggest this type of complex as a model for studying the interactions of core 4f electrons with conduction electrons.

Europium and ytterbium dissolve in liquid ammonia to give blue solutions.[3] We have found that Eu(bipy)$_4$, Yb(bipy)$_4$, and Yb(*o*-phen)$_4$ can be prepared by the reaction of bipyridyl or *o*-phenanthroline with the appropriate metal in liquid ammonia using the method reported for the preparation[4] of Ba(bipy)$_4$. After removal of the ammonia, the complex was dissolved in tetrahydrofuran and filtered. Removal of the tetrahydrofuran under high vacuum gave the unsolvated complex. *Anal.* Calcd for Yb(bipy)$_4$: Yb, 21.69; N, 14.05. Found: Yb, 21.7; N, 14.0. Calcd for Eu(bipy)$_4$: Eu, 19.57; N, 14.43. Found: Eu, 19.5; N, 14.4. Calcd for Yb(*o*-phen)$_4$: Yb, 19.36; N, 12.54. Found: Yb, 19.4; N, 12.6. The magnetic susceptibilities of the above complexes were measured in tetrahydrofuran by an nmr method.[5,6] TMS was used as the internal and external reference.[7] The magnetic moments of Yb(bipy)$_4$ and Yb(*o*-phen)$_4$ at 34° were found to be 2.79 and 2.78 BM, respectively.

These magnetic moments correspond to two unpaired electrons based on the spin-only formula for $J = 1$, $\mu = g\sqrt{J(J + 1)} = 2.83$ BM. Similar results[4] have been obtained by Herzog for Ba(bipy)$_4$. The triplet-state electron spin resonance[8] of complexes of the alkaline earths with bipyridyl and similar ligands indicates that formally low-valent metal complexes of electropositive metals are to be viewed as dipositive metal ions coordinated to radical anion-like ligands. Accordingly the presence of two unpaired electrons in Yb(bipy)$_4$ and Yb(*o*-phen)$_4$ suggests that the two 6s electrons of ytterbium metal have been transferred to the ligands.

The known close similarity of europium, ytterbium, and the heavier alkaline earths[9] indicates that Eu(bipy)$_4$ would have nine unpaired electrons, two on the radical anion-like ligands and seven in the shielded 4f subshell of the Eu^{2+} ion. The magnetic moments at different temperatures which we found for Eu(bipy)$_4$ are given in Table I. The magnetic moments calculated from the spin-only formula for five, seven, and nine unpaired electrons are 5.92, 7.94, and 9.95, respectively. We attribute the low magnetic moment of the europium complex to an antiferromagnetic exchange coupling between the 4f^7 electrons of Eu^{2+} and the two unpaired electrons on the ligands. A simple bonding explanation for the low magnetic moment is not plausible in that it is known that the 4f electrons are well shielded from the ligands by the 5s^{2}5p^6 shell. Our observation is apparently the first case of intramolecular antiferromagnetism where the exchange is between metal nonbonding electrons and unpaired electrons on the ligands. A useful analogy may be to view the electrons on the ligands as localized conduction electrons.

Table I. Magnetic Moments of Eu(bipy)$_4$

Temp, °K	μ_{eff}, BM[a]	Temp, °K	μ_{eff}, BM[a]
211	5.68	269	5.67
218	5.70	273	5.67
234	5.65	294	5.70
253	5.69	304	5.74
261	5.64	317	5.80

[a] Calculated from $\mu = 2.84\sqrt{\chi_m T}$ BM.

In the coupling of the two systems of electrons, J, the total angular momentum quantum number may take on all half-integral values[10] between $|J_{Eu^{2+}} + J_{ligand}|$ and $|J_{Eu^{2+}} - J_{ligand}|$, namely $^9/_2$, $^7/_2$, and $^5/_2$. In the antiferromagnetic scheme, the $^5/_2$ state will lie lowest. The near-constancy of the magnetic moments in Table I suggests that the $^7/_2$ and $^9/_2$ states are relatively unimportant at these temperatures. Therefore the exchange coupling must be strong and the Néel temperature must be well above room temperature. However, the results in Table I are related to the experimental observable

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through a square-root function, and the small positive deviation at higher temperatures is thought to be real.

The fact that the magnetic moments reported for the europium complex are slightly below that expected for a $J = {}^5/_2$ system may be a consequence of a slight shift in the *g* value. Such a shift has been noted for the $4f^7$ Gd^{3+} ion in metallic gadolinium and attributed to an interaction of the core electrons with the conduction band electrons.[11]

Further studies of the magnetic susceptibility and electron spin resonance of these and similar complexes are in progress.

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Enhancement of Biacetyl Luminescence by Deuteration[1,2]

Sir:

The mechanism of radiationless transitions between electronic states has been the subject of considerable theoretical[3] and experimental[4] study. Since nonradiative, rather than radiative, transitions are lifetime determining for many molecules of photochemical interest,[5] knowledge regarding the detailed nature of how one electronic state passes radiationlessly to another electronic state is crucial for the proper understanding of photochemical efficiencies.

Available theories emphasize either the intramolecular[3a-c] or the intermolecular[3d] effects which determine the rates of radiationless conversions. It is theoretically[3a,6a] expected, and experimentally found,[4,6] that the substitution of deuterium for hydrogen lowers the rate constant for radiationless transitions substantially, but has only a minor effect on radiative rates.[7] However, this effect has not been observed in the condensed phases for any molecules if the states undergoing radiative interconversion are similar in energy.[7] Essentially all of the data published to date pertains to the effect of deuterium substitution on organic molecules in rigid media.[7] Since biacetyl emits both fluorescence[8] and phosphorescence[9] even in fluid solution,[10,11] we have selected this relatively unique case to study how radiationless processes are affected by deuteration, both internally and externally.

Tables I and II present our findings on the luminescence of $CH_3COCOCH_3$ (**1**-H) and $CD_3COCOCD_3$ (**1**-D) under various conditions.[12] The measured lifetimes agree with those in the literature, being higher than those previously[13] reported for **1**-H at 77°K and approaching the highest values reported in fluid solution.[14] We thus feel that adventitious quenchers are not playing a significant role in our measurements.

Table I. Deuterium Enhancement at 77°K[a]

Biacetyl concn, *M*	τ_p, msec	τ_p(deuterated), msec
0.10	2.40	3.32
0.05	2.48	3.35
0.01	2.42	3.41
0.005	2.57	3.30
0.058[b]	1.91	2.78
0.058[c]	2.05	2.82

[a] In 5:5:2 ether:isopentane:ethyl alcohol glass unless otherwise stated. [b] In 3:1 ether:isopropyl alcohol. [c] In 3:1 ether-d_{10}:isopropyl alcohol-d_8.

Table II. Deuterium Enhancement at 25°

Biacetyl concn, *M*	τ_p, msec	τ_p(deuterated), msec
0.05[a]	0.46	0.49
0.05[b]	0.46	0.61
0.01[a]	0.45	0.62
0.01[b]	0.53	0.77
0.005[a]	0.50	0.70
0.005[b]	0.56	0.82

[a] In benzene. [b] In benzene-d_6.

Salient features of our data are the *enhanced fluorescence and phosphorescence of* **1**-*D over* **1**-*H in* C_6H_6 *and the enhanced phosphorescence of both* **1**-*H and* **1**-*D in* C_6D_6. An increase in fluorescence is not expected for the $S_1(n,\pi^*) \rightsquigarrow T_1(n,\pi^*)$ crossing of biacetyl, because these states are separated in energy[15] by only 10 kcal/mole. Nonetheless, the fluorescence intensity of biacetyl increases by 50% upon deuteration in EPA at −198° and by 20% at 25° in benzene. An intermolecular deuterium enhancement of luminescence has not been previously observed for an organic molecule in solution and is surprising.[4b,16]

We have corroborated the enhancement of fluorescence of **1**-D or **1**-H by direct lifetime measurements[17]

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