ethylpyridinium bromide (EPB) in pure EG. A similar plot for DPB in 40 vol % EG is also included in this figure, as DPB is known to form micelles in this solvent mixture.[11] A comparison of curve 4 with curves 1–3 indicates that the processes occurring in the two solvents are very similar. The positions of the cmc's on these curves are indicated by the arrows. The cmc so obtained for DPB in 40 vol % EG, 0.033 m, agrees well with the value, 0.0332 m, obtained by a spectrophotometric technique.[11,14,15] The cmc values are listed in Table I and are found to increase by factors of

Table I. Cmc Data at 27.5°

Detergent	Cmc in water,[a] m	Cmc in pure EG, m	Cmc_{EG}/cmc_{H_2O}
DPB	1.22×10^{-2} [b]	0.55	45
MTAB	3.84×10^{-3} [c]	0.25	65
CPC	9.2×10^{-4} [c]	0.23	250

[a] Calculated from the values at 25° assuming roughly 1% increases in going from 25 to 27.5°, which appears to be reasonable.[11] [b] References 15 and 11. [c] Reference 10.

45, 65, and 250 for DPB, MTAB, and CPC, respectively, in going from water to EG.

Unlike the long-chain (lc) electrolytes, ethylpyridinium bromide (EPB), a shorter chain analog of DPB, clearly raised the surface tension of EG (48.9), thus resembling NaCl in water[16a] in its behavior. This proves beyond any doubt that the pronounced surface activities of the lc electrolytes in EG are caused by the long hydrocarbon chains of these compounds, and not by any ion pairing, as the latter can be shown to occur to about the same degree in EPB and DPB in pure EG.[11]

However, a calculation of the surface excess,[16b] Γ_2, in the concentration region where there is the sharpest decrease in the surface tension, using the equation

$$\Gamma_2 = -\frac{1}{RT}\frac{d\gamma}{d \ln C} \tag{1}$$

shows that in 40 vol % EG Γ_2 is comparable to the values available for other detergents in water, whereas in pure EG these values are reduced by about a factor of 3. This would suggest that surface activity, although clearly existent, is considerably reduced in pure EG compared to that in water or 40 vol % EG.

An independent piece of evidence in favor of micelle formation in EG could be provided by the observation that at room temperature the solubility of CTAB in this solvent is lower by a factor of 10 or more than that of MTAB, although the hydrocarbon chain, supposed to be organophilic, is longer by two C atoms in the former. Also, preliminary measurements indicate that the solubility of CTAB in EG increases sharply in the temperature range 32–35°. This points to the possible existence in this solvent of a temperature similar to the Kraft temperatures known to exist for detergents in water.[16c]

The most likely conclusion will, therefore, be that micellar aggregation does take place in pure EG, although nothing is known yet as to how large these micelles are. To the knowledge of the present author, this is the first report ever made about the possible existence of micelles in any pure polar organic solvent.[17] More detailed investigations of this phenomenon are in progress in this laboratory.

(17) "Inverted" micelles are, however, known to form in some nonpolar solvents such as benzene, toluene, n-heptane, n-decane, etc.

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Molecular and Electronic Structure of μ-Nitrogen-decaamminediruthenium(II)

Sir:

The binuclear ruthenium complex [Ru(NH$_3$)$_5$N$_2$Ru-(NH$_3$)$_5$](BF$_4$)$_4$, recently isolated by Harrison, Taube, and Weissberger,[1] apparently contains molecular nitrogen as a bridging ligand and thus is of considerable theoretical interest. Not only does it serve as a simple model for the biological nitrogen fixation process, but it is of general importance in understanding the interactions between metal atoms and π-acceptor ligands. More particularly, it is an important link in the interesting class of binuclear compounds which contain simple diatomic bridging ligands such as O$_2^{-2}$ and CN$^-$.[3]

The crystals used in our study were prepared by the literature procedure.[1] Following the addition of KBF$_4$, the reactants were allowed to stand under N$_2$ for 4 days. After this period, small, golden yellow, octahedral crystals were found under an excess of KBF$_4$; a number were separated, washed with ethanol, and mounted on glass fibers for X-ray diffraction studies.

Weissenberg photographs (Cu Kα radiation) showed the crystals to be orthorhombic, the extinctions indicating the space group D$_{2h}^{15}$-Pbca. The cell constants are $a = 12.78$, $b = 15.53$, $c = 13.34$ Å. The observed density (flotation) of 1.96 g/cm³ is in good agreement with the value of 1.97 g/cm³ calculated for 4 dimeric cations, 16 BF$_4^-$ anions, and 8 water molecules per unit cell. In this space group, the cations must lie on centers of symmetry.

Intensity data for 3040 independent reflections were collected on a Datex-automated General Electric XRD-6 diffractometer, using zirconium-filtered Mo Kα radiation. The structure was determined by Patterson and Fourier methods and refined using full-matrix least-squares techniques. In the final cycles, all atoms except the hydrogens were assigned anisotropic temperature factors. The refinement proceeded to a final R factor ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.090 and a goodness of fit ($\Sigma w(F_o^2 - F_c^2/k^2)^2/(m - S)$)$^{1/2}$ of 1.63.

The dimeric cation is shown in Figure 1. The Ru-N$_2$Ru unit is very nearly linear (the Ru–N–N angle is 178.3 (5)°); the Ru–Ru distance is 4.979 (2) Å and

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Ru(1)–N(3) is 1.928 (6) Å. The N–N distance is 1.124 (15) Å, only slightly longer than that in free N_2 (1.0976 Å)[4] or N_2^+ (1.118 Å),[5] and well below the N–N distance in hydrazine (1.46 Å).[6] Five ammonia groups complete the octahedral coordination about each ruthenium, with the two equatorial sets in an eclipsed conformation (as required by symmetry). The apical N(9)–Ru(1) distance is 2.140 (6) Å, which is slightly longer than the average equatorial nitrogen–ruthenium bond length of 2.12 Å. One of the two BF_4^- groups in the asymmetric unit is either disordered or undergoing large thermal motion, so that accurate atomic positions could not be obtained. The other BF_4^- group is tetrahedral; the mean B–F distance is 1.34 Å.

The structure of the cation is in complete accord with infrared spectral results which show[1] only a very weak band in the 2050–2100-cm^{-1} region. In addition, recent Raman data have corroborated the linear nature of the Ru—N≡N—Ru unit.[7]

A preliminary model of the electronic structure of $Ru_2(NH_3)_{10}N_2^{4+}$ may be proposed for idealized D_{4h} symmetry; assuming that the important $Ru–N_2$ bonding involves the π^*N_2 level, we propose the molecular orbital ordering e_g $(xz_1 + xz_2, yz_1 + yz_2) < b_{2g}$ $(xy_1 + xy_2) \sim b_{1u}$ $(xy_1 - xy_2) < e_u$ $(xz_1 - xz_2, yz_1 - yz_2) < e_g(\pi^*N_2)$. In this formulation, the ground state is $(e_g)^4(b_{2g})^2(b_{1u})^2(e_u)^4 \equiv {}^1A_{1g}$. The π bonding from the two Ru centers to the N_2 is provided by the four electrons in the e_g level, giving an average of one π bond per Ru. In the reference mononuclear complex, $Ru(NH_3)_5N_2^{2+}$, which is known to have a linear RuN_2 unit,[8] the π-bond order is two and a somewhat shorter $Ru–(N_2)$ distance would be expected. Although accurate molecular parameters are not yet available for $Ru(NH_3)_5N_2^{2+}$, the fact that $[Co(H)(N_2)PPh_3)_3]$ shows[9] a metal-N_2 bond length of 1.8 Å may be taken as evidence that the π interactions per metal center have decreased in $Ru_2(NH_3)_{10}N_2^{4+}$. It is also interesting to note that the N–N distances in the two structures are not significantly different (1.11 Å in Co^I—N≡N,[9] 1.124 (15) Å in Ru^{II}—N≡N—Ru^{II}); again this observation is in accord with the crude theory because both mononuclear and binuclear systems furnish a total of four $d\pi$ electrons to the π^*N_2 level.

The intense absorption band at 263 nm (ϵ 4.8 × 10^4) which characterizes[1] the $Ru_2(NH_3)_{10}N_2^{4+}$ complex may be assigned to the allowed metal-to-ligand charge-transfer transition $e_u \rightarrow e_g$ (π^*N_2). The model allows a qualitative understanding of the much higher energy of the $Ru{\rightarrow}\pi^*N_2$ band in $Ru(NH_3)_5N_2^{2+}$. (The intense band is found[10] at 221 nm in the latter complex, which is ca. 7200 cm^{-1} higher than in the binuclear case.) The occupied d levels should be at relatively lower energy in $Ru(NH_3)_5N_2^{2+}$, because the partial withdrawal of four $d\pi$ electrons through $d\pi \rightarrow \pi^*N_2$ bonding leaves the central ruthenium with a larger effective positive charge than in the binuclear case. Thus, excitation of either
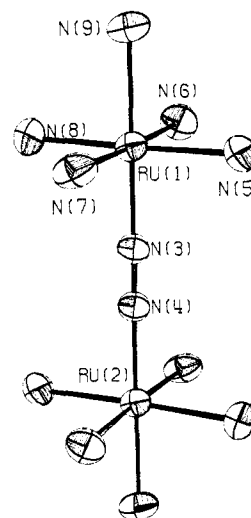

Figure 1. A view of the $Ru_2(NH_3)_{10}N_2^{4+}$ cation. The atoms are represented by ellipsoids whose principal axes were derived from the final values of the anisotropic temperature parameters.

a metal b_2 or e electron to $e(\pi^*N_2)$ in the C_{4v} mononuclear complex would require more energy than the $e_u \rightarrow e_g(\pi^*N_2)$ transition in $Ru_2(NH_3)_{10}N_2^{4+}$.

We conclude that a simple molecular orbital model which emphasizes the importance of $Ru{\rightarrow}\pi^*N_2$ π bonding is adequate as a basis for discussion of relevant bond parameters and the electronic spectra of $Ru_2(NH_3)_{10}N_2^{4+}$ and $Ru(NH_3)_5N_2^{2+}$.

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Photochromism of 1,2-Dihydroquinolines

Sir:

As a part of our continuing investigation of the spectroscopy and primary photochemical processes of molecules,[1] we wish to report photochemistry (photochromism) of the 1,2-dihydroquinolines. Their colorless solid solutions in EPA[2] at −196° develop color upon irradiation with ultraviolet light (1-kW Hg–Xe source, Corning glass filter 9863 transmitting approximately in the region of 250–390 nm).

The colored form can be eradicated thermally and the process can be repeated several times. Thus far, we have investigated six dihydroquinolines; five of them exhibited photochromic behavior. They are listed in Table I.[3]

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(1) For example, see R. S. Becker and J. Kolc, *J. Phys. Chem.*, **72**, 997 (1968), and references therein; A. Santiago and R. S. Becker, *J. Amer. Chem. Soc.*, **90**, 3654 (1968); R. S. Becker, E. Dolan, and D. E. Balke, *J. Chem. Phys.*, **50**, 239 (1969), and references therein.
(2) Ethyl ether, isopentane, and ethyl alcohol in volume ratio of 5:5:2, respectively.
(3) Compound 1 was synthesized in this laboratory according to H. Rupe, R. Paltzer, and K. Engel, *Helv. Chim. Acta*, **20**, 209 (1937), and recrystallized several times from ethanol. Compounds 3 and 4 were purchased from Aldrich Chemical Co.; compounds 2 and 5 (and also 1) were generously donated by Dr. F. D. Popp, Clarkson College of Technology, Potsdam, N. Y. Compound 6 was a kind gift from Drs. H. O. Huisman and W. N. Speckamp, University of Amsterdam, The Netherlands.