Table II. Calculated Relative Energies and Quadrupole Splittings for Model HRP-I and HRP-II Intermediates

	ΔE, eV	ΔE_Q, mm/s	η	V_{ii}^{max}
HRP-I ($S = ^3/_2$)				
Fe(V) ($S = ^3/_2$) por π ($S = 0$)	1.100	1.64	0.27	V_{yy}
Fe(IV) ($S = 2$) por π ($S = ^1/_2$)	1.358	−0.89	0.12	V_{zz}
Fe(IV) ($S = 1$) por a_{1u} π ($S = ^1/_2$)	0.000	1.43	0.02	V_{zz}
Fe(IV) ($S = 1$) por a_{2u} π ($S = ^1/_2$)	0.354	1.43	0.01	V_{zz}
Fe(III) ($S = ^5/_2$) por π ($S = -1$)	0.849	0.34	0.24	V_{zz}
Fe(III) ($S = ^1/_2$) por π ($S = 1$)	0.649	−2.65	0.20	V_{zz}
HRP-II ($S = 1$)				
Fe(IV) ($S = 1$) por π ($S = 0$)	−5.825	1.51	0.02	V_{zz}
Expt[a]				
HRP-I		1.38	0	V_{zz}
HRP-II		1.44	0	V_{zz}

[a] See ref 10.

density resides primarily on the α and methine carbon atoms. In neither configuration is there a significant amount of spin density of any C_β atom, including the four $C_{\beta'}$ atoms which have the methyl substituents in protoporphyrin heme units. Addition of substituents to the porphyrin ring does not appreciably change the spin density in these π orbitals.[17] Neither the resting states nor the model HRP-II has a significant amount of spin density on these β carbon atoms. However, both the resting state and HRP-I have significant π spin density on the C_α and C_m carbon atoms, in contrast to HRP-II which has no spin density on these atoms. These results are consistent with the fact that the observed CH_3 proton chemical shift in NMR spectra is similar for the resting state and HRP-I and different for HRP-I and HRP-II.

Thus, the observed NMR results are completely consistent with a description of HRP-I as a Fe(IV) ($S = 1$) por π ($S = ^1/_2$) radical, with either a_{1u}- or a_{2u}-type spin density on the porphyrin π ring and with the a_{2u} π cation structure for normal and the a_{1u} π cation structure for reconstituted deuteroheme HRP-I. Furthermore, the spin densities calculated for the a_{2u} π and a_{1u} π cation radical structures are consistent with the characteristic ESR parameters observed for the two types of radicals, i.e., ESR spectra in keeping with high spin density at the methine carbon positions and nitrogen splittings in the former and small spin density at the methine carbon positions and no resolved nitrogen splittings in the latter.[18]

To further investigate the plausibility of these electronic structures for HRP-I, we have calculated the relative energies, electric-field gradients at the iron nucleus, and quadrupole splittings for them as well as for a number of other previously proposed electronic structures for HRP-I: Fe(V) (d^3, $S = ^3/_2$), with all oxidizing equivalents and unpaired spin density localized on the iron; Fe(IV) (d^4, $S = 2$), a high-spin variation of the iron(IV) state as suggested by Morishima and Ogawa,[11] but with the spin-coupled electron on the porphyrin ring; and high-spin Fe(III) (d^5, $S = ^5/_2$) and low-spin (d^5, $S = ^1/_2$) Fe(III) states of model HRP-I, with both oxidizing equivalents and unpaired electrons on the porphyrin ring rather than on the iron.

The spin densities calculated for all of these states are compatible with the observed ^{1}H NMR of HRP and HRP-I, i.e., little or no spin density on $C_{\beta'}$ atoms. Table II gives the relative energies and quadrupole splittings calculated for each of these electronic configurations. We see from this table that the Fe(IV) (d^4, $S = 1$) por a_{2u} π ($S = ^1/_2$) and Fe(IV) (d^4, $S = 1$) por a_{1u} π ($S = 1$) states both have very similar quadrupole splittings and are in best agreement with experiment. Furthermore, both the a_{1u} and a_{2u} cation radicals have similar energies, with the a_{1u} cation radical predicted to be the lowest energy state. This behavior may certainly be correct for the unsubstituted porphyrin ring used in these calculations. Recent electronic spectra[19] and ^{1}H NMR studies[11] of both normal HRP-I and HRP-I reconstituted with deuterohemin demonstrate the sensitivity of an a_{1u} vs. an a_{2u} π cation to ring substituents. The protoporphyrin HRP-I appears to be an a_{2u}-type radical[3] and the deutero HRP-I an a_{1u}-type radical.[19] Our results indicate how close these two states are in energy and suggest that if reconstituted HRP-I were prepared with simple porphine heme an a_{1u} cation radical would be obtained.

Of the other possible configurations, only the (d^3, $S = ^3/_2$) Fe(V) state of the model HRP-I yields a value of ΔE_Q consistent with the observed value. However, for this state, the principal value of the electronic-field gradient at the iron nucleus is predicted to be in the heme plane rather than perpendicular to it. Mössbauer resonance experiments on oriented samples are suggested to determine the principal direction of the field gradient to help distinguish between an Fe(IV) and an Fe(V) structure.

We have also calculated the electronic structure and quadrupole splittings for a model of HRP-II. The most favorable HRP-II has a (d^4, $S = 1$) Fe(IV) electronic structure with no porphyrin π cation character. As seen in Table I, the calculated value of ΔE_Q for this state is in good agreement with experiment,[8-10] and the lower energy of HRP-II compared to HRP-I is consistent with the facile reduction observed.

The results presented here, together with other experimental and theoretical evidence, now point to an Fe(IV) (d^4, $S = 1$) por a_{2u} π ($S = ^1/_2$) cation as the most plausible electronic state of HRP-I. The ^{13}C and ^{15}N NMR studies recently suggested by investigators[11] should be very useful in verifying the π cation nature of HRP-I and the sensitivity of an a_{1u} or a_{2u} ground state to porphyrin ring substituents, which is strongly suggested by ours and other existing results. Such studies would directly link observed peak positions and line widths to calculated values of spin densities for a_{1u}- and a_{2u}-type cation radicals and, hence, further aid in distinguishing between such radicals. These experiments would also help determine which theoretical method, if any, gives the more reliable quantitative correlations to observed frequency shifts and line broadening.

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Gas-Phase Complexes of Cu^+ and Ag^+ via Thermionic Emission Sources

Sir:

The gas-phase clustering of molecules about ions can provide important information about both solvation phenomena and the chemistry of gas-phase complexes. Although the coordination complexes of transition-metal ions have been extensively studied in solution, relatively few studies involving transition-metal-ion complexes have been carried out in the gas phase. These ICR studies have been mostly limited to complexes that can be generated via electron-impact fragmentation of volatile inorganic compounds.[1] The most recent development in ICR work involving

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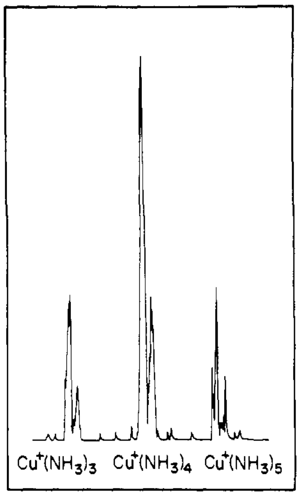

Figure 1. Mass spectrum of $Cu^+(NH_3)_n$ clusters at 7-torr pressure of ammonia. The ^{63}Cu and ^{65}Cu isotopes are evident in each cluster peak.

transition-metal ions (copper) has been the use of laser vaporization of the metal to produce ions.[2] These techniques are less than ideal, the first due to the complicating presence of unwanted fragment ions, and the second due to the excess kinetic energy of laser-generated ions.

We report that it is possible to generate transition-metal ions by thermionic emission and that we are currently using Cu^+ and Ag^+ filaments in our laboratory for studies of ion clustering with water and ammonia as ligands. The general method we use for the preparation of thermionic emission filaments has been described earlier in this journal.[3] In the case of the Cu^+ and Ag^+ filaments described above, the procedure is particularly dependent on the use of high-purity starting materials[4] followed by several hours of operation during which alkali metal ion impurities are baked out. The resulting filaments have only trace alkali metal impurities, and we have found them to be suitable for several weeks of almost continuous use.

The solvation structure and coordination of ligands about ions are areas of particular interest in our research program. Burnier et al.[2] have suggested that no distinct inner- and outer-coordination spheres are apparent in the ΔH values of alkali metal ions clustered by ligands such as H_2O, NH_3, and CH_3CN. We point out work carried out in our laboratory on the clustering of ammonia about alkali metal ions[3,5] and, in particular, evidence that well-defined "coordination shells" may exist for the Li^+ and Na^+ systems.[3] Other evidence of possible "coordination" in the gas phase is shown in ΔH plots of water about Sr^+ ion[6] and NH_4^+ ion[7] which suggest that they are 8- and 4-coordinate, respectively. It is likely that the apparent "coordination" in the gas phase for some systems reflects a special "fit" of ligands about the central ion to form a highly ordered structure. This is unlike the case for many ion clusters where less ordered structures similar to those obtained in Monte Carlo calculations[8] are probable.

Studies of clustering about transition-metal ions should provide particularly useful information relevant to coordination phenomena since many coordination complexes are known to exist in solution. This is because in gas-phase clustering studies the binding of additional ligands, beyond those of the known coordination complex in solution, can be examined. For example, the mass spectrum in Figure 1 shows the Cu^+ ion with 3, 4, and 5 ammonia ligands whereas in solution the coordination complex $Cu^+(NH_3)_2$ occurs. It has been suggested in an earlier study that the third ammonia ligand has an intrinsically weak interaction.[2] Our results show that while the third, fourth, and fifth ammonia ligands in $Cu^+(NH_3)_n$ bind less strongly than the corresponding water ligands in $Cu^+(H_2O)_n$, they each have binding energies in excess of 10 kcal/mol. In particular, equilibrium measurements have been used to determine requisite binding energies for the reactions of M^+ (M = Cu, Ag) with ammonia, represented by eq 1 (n = 2-4).

$$M^+\cdot(NH_3)_n + NH_3 \rightleftharpoons M^+(NH_3)_{n+1}$$

The standard enthalpy values for copper are 14.0, 12.8, and 12.8 kcal/mol, respectively, while those for silver are 14.6, 13.0, and 12.8 kcal/mol. This demonstrates that ligands beyond the "coordination" complex (with two ligands) still have significant binding energies (even though binding in the coordination complexes is well in excess of 30 kcal/mol). The observed $Cu^+(NH_3)_2$ species in solution is probably due to preferential bonding of the ion to solvent beyond the second ligand, rather than to an intrinsic inability to bind additional ligands.

Gas-phase clustering about transition-metal ions is a promising new area of chemistry which should offer important information and insights relevant to both the study of coordination complexes and solvation phenomena.

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Fluxional Behavior of $[Rh_{14}(CO)_{25}H_{4-n}]^{n-}$ (n = 3 and 4)

Sir:

The carbonyl cluster anions $[Rh_{13}(CO)_{24}H_{5-x}]^{x-}$ (x = 3 and 2) exhibit carbonyl migration on the outside and H migration on the inside of the hexagonal close-packed metal skeleton;[1] *both* migrations necessitate the involvement of all twelve outer rhodium atoms. Recent work[2] has shown that the activation energies for carbonyl and H migrations are similar, and it thus seems probable that the migratory motions of both ligands are interrelated. We now report on the fluxional behavior of $[Rh_{14}(CO)_{25}H_{4-n}]^{n-}$ (n = 4 and 3); the monohydride provides a second example of interstitial H migration, but in this case, the hydrogen migrates to rhodium atoms which are *not* involved in carbonyl rearrangements.

The X-ray structures of $[Rh_{14}(CO)_{25}]^{4-}$ and $[Rh_{14}(CO)_{25}H]^{3-}$ are very similar[3,4] and are shown schematically in Figure 1. A well-resolved ^{13}C NMR spectrum of $[Rh_{14}(CO)_{25}]^{4-}$ in EtCN was obtained on lowering the temperature to -60 °C. This is shown in Figure 2e together with the assignments which have been established by $^{13}C-^{103}Rh$ NMR studies. Thus, irradiation at 3.156847 MHz [δ (^{103}Rh) -1001[5]] collapses only the quintet at

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