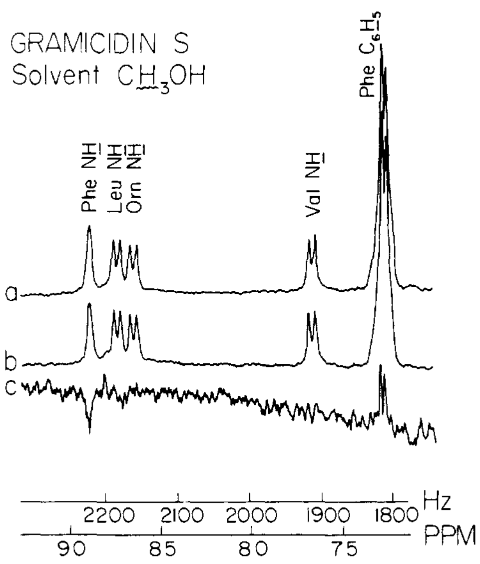

Figure 3. Solvent saturation study of gramicidin S in methanol showing the effect of saturation of the solvent CH_3 peak. Conditions are the same as in Figure 2 except that the CH_3 resonance rather than the OH resonance of methanol is saturated. The amplification factor in (c) is 5.

When the CH_3OH resonance is saturated, the intensity of the Phe C_6H_5 resonance is increased by 5 ± 1%, while the intensity of the Phe NH peak is diminished by 8 ± 2% (Figure 3). The positive NOE experienced by the ring protons results from dipole-dipole interaction between solvent CH_3 protons and phenyl hydrogens. The inverse sixth power dependence of dipolar coupling on internuclear distance[14] indicates intimate contact between the hydrophobic Phe ring and solvent methyl groups. The decreased intensity of the Phe NH resonance results from transfer of magnetization from the CH_3OH proton, which, as indicated in Figure 2, is exchanging rapidly with the Phe NH proton. The methanol OH resonance decreases in intensity by 22% upon saturation of the CH_3 peak, because the hydroxyl proton is relaxed by exchange modulation of its scalar coupling with the methyl hydrogens.[14]

The solvent saturation experiment was repeated in the highly polar solvent, dimethyl sulfoxide. Saturation of the solvent methyl resonance results in a nuclear Overhauser enhancement of 10 ± 1% for the Phe ring protons, suggesting intimate contact between methyl protons and ring CH protons, as was similarly suggested for the methyl group of methanol. Since dimethyl sulfoxide has no exchangeable hydrogens, no perturbation is observed in the intensities of the other resonances. The Orn primary NH_2 resonance was not observed probably because a trace amount of H_2O exchange-broadened this resonance beyond detection.

In TFE an enhancement of 5 ± 1% for the Phe C_6H_5 peak is seen when the solvent ^{19}F resonance is saturated. Irradiation of the methylene or hydroxyl protons of TFE produces no intensity changes in the spectrum of gramicidin S. Even though TFE has an exchangeable OH proton, no transfer of saturation is observed, because of the slow exchange rate of this proton.[13] These observations indicate that in TFE the trifluoromethyl group is closer to the Phe C_6H_5 protons than either the methylene or hydroxyl group.

The intermolecular NOE's are small because of competitive relaxation of the Phe ring protons by mechanisms other than intermolecular dipole-dipole interaction with the solvent. It is likely that these competitive mechanisms are predominantly intramolecular dipolar interactions, which would be enhanced by proximity of solute hydrogens and long intramolecular correlation times. These intramolecular mechanisms could be diminished by selective deuteration of gramicidin S. Other mechanisms, although less likely, cannot be excluded; however, dissolved oxygen does not significantly relax the ring protons, since degassing of samples had no effect on the NOE's. It is evident that the solvent saturation method has considerable potential for elucidating the details of solute-solvent interactions.

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The Mononuclear Nature of the Aquomolybdenum(IV) Ion in Solution

Sir:

Two groups have reported the preparation of the aquo ion of molybdenum(IV) in solution. Souchay and coworkers[1,2] favor a monomeric assignment, while in a later study Ardon and Pernick[3] concluded that the aquo ion is dimeric at $[H^+] > 1\ M$. Using a variety of techniques we have been able to show that the aquo ion exists as a monomeric 2+ species, MoO^{2+} (or possibly $Mo(OH)_2{}^{2+}$) over the $[H^+]$ range 0.3-2.0 M investigated, in agreement with Souchay et al.[2]

Prior to 1966 molybdenum(IV) was thought to be unstable in aqueous solution.[4,5] It has not for example been possible to obtain chloromolybdenum(IV) complexes in aqueous media, and chloro complexes as well as the thiocyanato complex $Mo(NCS)_6{}^{2-}$ disproportionate to molybdenum(III) and molybdenum(V).[6] Even the usually very stable $K_4[Mo(CN)_8]$ undergoes disproportionation in concentrated HCl.[7] The only molybdenum(IV) complexes which have been isolated from aqueous solution are the oxalates, $(NH_4)_4[Mo(oxal)_4]$,[8] $M_2[Mo_3O_4(oxal)_3(H_2O)_5]$ (M = K, pyH),[9] and the poorly characterized species $[MoO(oxal)(H_2O)_3]_n$,[10] and various cyano complexes.[4]

In 1973 Ardon and Pernick,[3] reported what they believed to be the first preparation of a stable aquo ion of molyb-

Table I. Summary of Data for the Thiocyanate Complexing with the Mo(IV) Aquo Ion (which allow an assignment of a monomeric and not dimeric structure to the latter; temp 25°, $I = 2.0\ M$ ($LiClO_4$))

	Excess NCS^-		Excess Mo(IV)	
Parameter	Monomer assumed	Dimer assumed	Monomer assumed	Dimer assumed
k_f(M^{-1} sec^{-1}), $[H^+] = 2.0\ M$	0.76 ± 0.04	0.76 ± 0.04	0.70 ± 0.05	1.40 ± 0.10
k_f(M^{-1} sec^{-1}), $[H^+] = 1.0\ M$	1.45 ± 0.10	1.45 ± 0.10	1.68 ± 0.10	3.36 ± 0.20
K_1(kin) (M^{-1}), $[H^+] = 2.0\ M$	350 ± 35	350 ± 35	350 ± 65	700 ± 130
K_1(kin) (M^{-1}), $[H^+] = 1.0\ M$	390 ± 60	390 ± 60	540 ± 80	1080 ± 160
K_1(spec) (M^{-1}), $[H^+] = 2.0\ M$	430 ± 35	430 ± 35	520 ± 45	1040 ± 90
ϵ(M^{-1} cm^{-1}), λ 370 nm	2700 ± 100	5400 ± 200	2970 ± 150	2970 ± 150

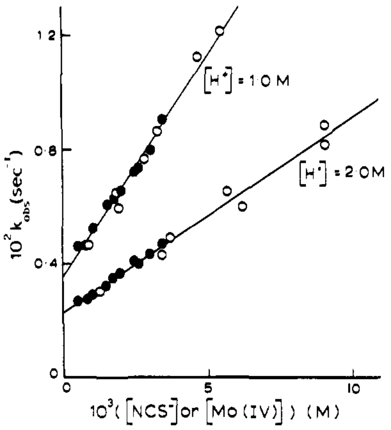

Figure 1. Demonstration of the monomeric nature of the Mo(IV) aquo ion based on kinetic studies (25°) of the equilibration with thiocyanate, $[NCS^-]$ (●) or [Mo(IV)] (○) in excess, $I = 2.0\ M$ ($LiClO_4$).

denum(IV). Based on redox titration results, charge per Mo determinations and the observation that the ion was eluted only slowly from cation exchange resins even with 2 *M* $HClO_4$, they concluded that the species was a 4+ dimer. In fact, as Ardon and Pernick later acknowledged,[11] the aquo ion of molybdenum(IV) had been prepared previously, using a similar method of preparation (heating molybdenum(III) and molybdenum(V) at 80-90° for 1-2 hr) by Souchay et al.[1,2] Using cryoscopic spectroscopic and potentiometric techniques the latter concluded that the pink aquo ion was monomeric and dipositive, and assigned a formula MoO^{2+}. Souchay and coworkers have also obtained evidence for other Mo(IV) species in aqueous solution[12] including thiocyanates,[13] tartrates,[14] and even the ion MoO_3^{2-},[2] which is stable in very basic solution.

In the course of a study[15] on the kinetics of equilibration of thiocyanate with aquo Mo(IV), $[H^+] = 0.75$-$2.0\ M$, it has become clear to us that the species is indeed monomeric. A monothiocyanato complex is formed under the conditions studied, and the formation can be expressed as in eq 1.

$$(Mo^{IV})_n + NCS^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} (Mo^{IV})_nNCS \qquad (1)$$

At constant $[H^+]$ the pseudo-first-order rate constant, k_{obsd}, for the equilibration (1) is given by eq 2

$$k_{obsd} = k_f([(Mo^{IV})_n] \text{ or } [NCS^-]) + k_b \qquad (2)$$

where $[(Mo^{IV})_n]$ or $[NCS^-]$ is relevant depending on whether Mo(IV) or NCS^- is in large (>10×) excess. With thiocyanate in excess, plots of k_{obsd} against $[NCS^-]$ yield unambiguously k_f and k_b, whereas for excess Mo(IV), the degree of polymerization, *n*, is important. It is possible to assume values of *n* in eq 2 and see which gives the best correspondence to the data with excess thiocyanate. From Figure 1 it can be seen that an excellent fit is obtained with a value of $n = 1$. Hence it is concluded that Mo(IV) is monomeric in aqueous solution with $[HClO_4] = 1.0$ and $2.0\ M$. A value of $n = 1$ is also required for satisfactory correspondence of equilibrium constants, K_1 ($= k_f/k_b$), derived from both kinetic and spectrophotometric measurements, and also of absorption coefficients (ϵ) for the product; see Table I. Ion-exchange separation and analysis of the reaction product have revealed Mo:NCS ratios of 1:0.95.

We have also determined the charge per aquo ion, using the ion-exchange method of Cady and Connick (here Dowex 50 W-X12 resin was used).[16] From two determinations, one with $HClO_4 = 0.75$ and $1.5\ M$, and the other 0.5 and 1.0 *M*, a value of 2.08 ± 0.07 was obtained. The charge per Mo was estimated by a modified frontal analysis approach.[17] A column of Dowex 50W-X8 cation exchange resin (4 × 0.6 cm) of known capacity in the H^+ form was brought as close as possible to saturation by treating with a large excess of Mo(IV), $[H^+] = 0.5\ M$, and then again with a solution of Mo(IV), $[H^+] = 0.3\ M$. Since Mo(IV) is not eluted by 0.5 *M* $HClO_4$, saturation of the resin by Mo(IV) is almost certainly >90% complete. The resin was washed with water to remove free Mo(IV), and the Mo(IV) was eluted with 2 *M* H^+ using $HClO_4$ or *p*-toluenesulfonic acid (HPTS), and then titrated against Ce(IV) with ferroin as indicator. The last traces of Mo(IV) on the resin were estimated by treating the resin with a solution containing excess aquo Fe(III), followed by addition of an equimolar amount of ethylenediaminetetraacetate (EDTA), which complexed the unreacted Fe(III). The remaining uncomplexed EDTA was then titrated against Bi(III) using Xylenol Orange as indicator. From the resin capacity and the total amount of Mo(IV) a charge per Mo atom of 2.20 was obtained. This should be regarded as an upper limit since the column was not completely saturated. A value of $n = 0.95$ is obtained from the ratio of the charge per ion to the charge per Mo. These results confirm the monomeric nature of Mo(IV) and indicate that the ion is a divalent cation, most probably MoO^{2+}, as suggested by Souchay et al,[2] or perhaps less likely $Mo(OH)_2^{2+}$. Ardon and Pernick[3] assigned the binuclear structure on the qualitative observation that it was eluted only slowly by 2 *M* $HClO_4$ from Dowex 50W-X2 resin. We observe similar ion-exchange behavior, and it appears that for the heavier metal oxo cations care is required in basing structural assignments on ion-exchange elution behavior.

We have also isolated a solid containing aquomolybdenum(IV) by the addition of 0.75 equiv of $K_4[Mo(CN)_8]$ to ca. 3 *M* HPTS solution containing the aquo ion. On mixing the reactant the color of the aquo Mo(IV) solution changed from pink to deep red. Addition of 6 volumes of absolute ethanol precipitated a deep purple brown microcrystalline solid which was filtered off, washed with ethanol and ether, and after drying was immediately analyzed. Titration of freshly prepared solutions with Fe(III) (aquo Mo(IV) is oxidized to Mo(VI), but $Mo(CN)_8^{4-}$ remains unchanged) and Ce(IV) (aquo Mo(IV) is oxidized to Mo(VI), and $Mo(CN)_8^{4-}$ to $Mo(CN)_8^{3-}$) revealed an aquo Mo(IV): $Mo(CN)_8^{4-}$ ratio of 1:1.02. In addition analyses for C and

N indicated a composition Mo(IV) (total):CN^- of 1:3.96 with all C and N present as CN^-. It was demonstrated that the oxidation state of the aquomolybdenum remained (IV) by determination of the ratio of Fe(III) needed for oxidation of the molybdenum before and after reduction by Zn/Hg to Mo(III) (air-free techniques required). These results show that the solid obtained is a 1:1 adduct of aquo Mo(IV) and $Mo(CN)_8{}^{4-}$. Flame photometry revealed the presence of about one K^+ per aquo Mo(IV) indicating the possibility of one H^+ in the solid. Analysis figures were reproducible to ±5% for different samples and a ratio aquo Mo(IV):$Mo(CN)_8{}^{4-}$:CN^- of 1:1:8 was obtained in all cases. The solid is only stable for periods <3 hr. It is weakly acidic, a 1.25×10^{-3} *M* solution giving a pH of 3.08. The ir spectrum gives a broad ν(C=N) stretch at 2125 cm^{-1}. The lack of any shift compared to $K_4[Mo(CN)_8]$ indicates that CN^- bridging of the two molybdenum centers is probably absent.

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Intrinsic Acid-Base Properties of Molecules. Binding Energies of Li^+ to π- and n-Donor Bases

Sir:

The intrinsic basicity of a molecule B may be quantitatively specified by its binding energy to a reference acid in the gas phase. Proton binding energies (eq 1) have been obtained for a large number of organic and inorganic species,[1] providing one scale of molecule basicity. We wish to report the determination of the binding energies of 30 π- and n-donor bases to the reference acid Li^+ (eq 2) and the comparison of two scales of molecular basicity afforded by these results.

$$BH^+ \rightarrow B + H^+ \qquad \Delta H = D(B\text{-}H^+) \equiv PA(B) \quad (1)$$

$$BLi^+ \rightarrow B + Li^+ \qquad \Delta H = D(B\text{-}Li^+) \quad (2)$$

We have recently demonstrated that bimolecular reactions of alkali ions with certain alkyl halides lead to the formation of complexes of these species with molecules.[2] For example, Li^+ reacts with isopropyl chloride to form the complex of Li^+ with propylene (reaction 3). Transfer of Li^+ between molecules (reaction 4) is rapid allowing examination of the relative binding energies of Li^+ to various bases by use of trapped ion cyclotron resonance (ICR) techniques.[3,4]

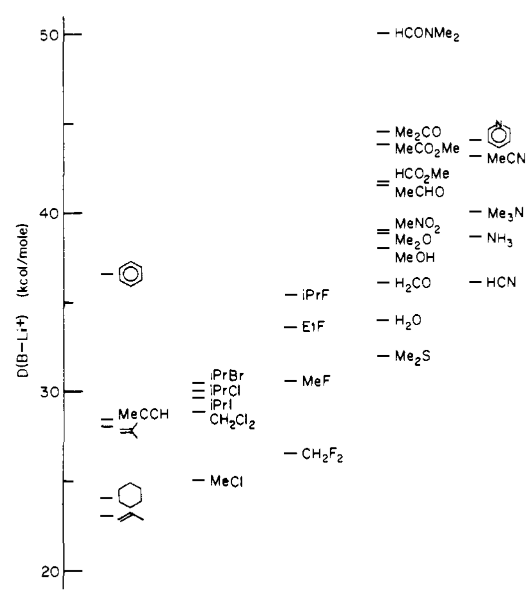

Figure 1. Binding energies of molecules to Li^+.

$$(CH_3)_2CHCl + Li^+ \rightarrow (CH_3CH{=}CH_2)Li^+ + HCl \quad (3)$$

$$B_1Li^+ + B_2 \rightleftharpoons B_1 + B_2Li^+ \quad (4)$$

Relative values of $D(B\text{-}Li^+)$ are quantitatively determined in cases where the free energy change for reaction 4 is sufficiently small (<3 kcal/mol) that equilibrium constants can be obtained.[1] A scale of Li^+ binding energies (Figure 1) has been constructed by combining the results of such determinations[5] and is referenced to experimental[6] and theoretical[7] values for $D(H_2O\text{-}Li^+) = 34$ kcal/mol. Relative to H_2O, reported values are estimated to be accurate to ±2 kcal/mol, with higher accuracy for smaller differences.

Several points may be noted in examining the data of Figure 1. Molecular binding energies of Li^+ are substantial even for a saturated species such as cyclohexane, $D(B\text{-}Li^+) = 24$ kcal/mol, and become quite large for aromatics, $D(C_6H_6\text{-}Li^+) = 37$ kcal/mol. $D(B\text{-}Li^+)$ increases with methyl substitution at the basic site in both π- (isobutene > propene) and n-donor bases ($Me_2O > MeOH > H_2O$, $Me_3N > NH_3$). Greater basicity toward Li^+ also results from increasing the size of the alkyl substituent (*i*-PrF > EtF > MeF). Compared to first-row species $D(B\text{-}Li^+)$ is smaller for second-row n-donor bases ($MeCl < MeF$, $Me_2S < Me_2O$).

These results may benefit theoretical approaches to the understanding of alkali ion interactions with molecules. The interaction potential has been described both at short distances where scattering results have been used to characterize the repulsive part of the potential[8] and at long distances where electrostatic terms dominate.[9] The present data describe the interaction at the equilibrium configuration. They provide quantification of the energetic changes associated with reactions in which alkali ions are involved both in the gas phase and solution and may be used to interpret the specific binding of alkali ions by polyfunctional molecules and in biological systems.[10] In addition, the data are directly applicable to the development of chemical ionization sources using alkali ions.[11]