Reactions of Gas-Phase Atomic Metal Ions with the Macrocyclic Ligand Tribenzocyclotriyne

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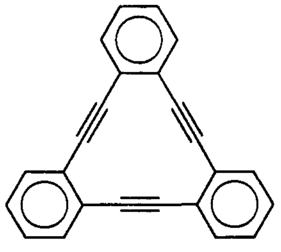
Abstract: Reactions of 22 atomic metal cations with the macrocyclic molecule tribenzocyclotriyne (TBC) were studied in the gas phase in the Fourier-transform ion cyclotron resonance spectrometer. Most of the ions underwent association with TBC with good collisional efficiency to give $M(TBC)^+$, with the exceptions of Zn^+ and Au^+, for which the highly exothermic charge-transfer reaction dominated, and Cs^+, which was unreactive. Most of the $M(TBC)^+$ ions attached a second ligand to give $M(TBC)^{2+}$, presumably the sandwich complex. Cases for which sandwich formation was slow or negligible included several late first-row transition metal ions which probably insert into the TBC cavity, and several other ions (K^+, Al^+, Pb^+) which apparently have poor electronic interaction with the ligand. Periodic trends for both complexation reactions are discussed, and a rationale is advanced for the surprising inefficiency of exothermic charge transfer in most cases.

Introduction

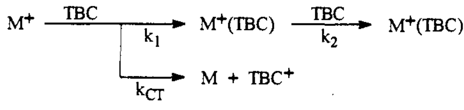
Studying the association chemistry of metal ions with macrocycles and other chelating ligands has particular interest in the gas phase. For the synthetic chemist, the patterns of particular stability of the metallomacrocycles observed in the gas phase, where solvent chemistry and other secondary processes are not present, can be a valuable guide to synthetic targets and strategies in solution. From the point of view of understanding the systematics of chemical bonding, the patterns of ion–ligand interactions seen in the gas phase give a baseline of solvent-free and packing-force-free information complementary to solution and crystallographic studies. Finally, with respect to reactivity, the reactions of simple atomic ions with large, polarizable, anisotropic ligands offer uniquely interesting problems in understanding ion–neutral reaction kinetics, dynamics, and interactions.

An earlier publication[1] described initial studies of the reactions of some transition metal ions with the novel ligand tribenzocyclotriyne (TBC), a highly conjugated antiaromatic planar molecule with a central cavity of size comparable to atomic ion dimensions. The ions were found to react by radiative association, with an exceptional absence of complications, to form M^+L and M^+L_2 complexes. A striking regular variation across the periodic table was observed in the extent of formation of the "sandwich" M^+L_2 complexes. The attempt to understand this pattern, which shows provocative parallels to condensed-phase complex formation,[2–4] impelled us to an expanded exploration of this chemistry, extending over a wider range of the metallic side of the periodic table.



TBC

The sequential addition of two TBC molecules to the metal ion was described and analyzed in ref 1. It has since become clear that the charge transfer from M^+ to TBC is an additional, competing reaction channel for some metal ions, and the complete kinetic scheme considered in this study can be written



$$\begin{tikzcd} M^+ \arrow[r, "TBC", "k_1"'] \arrow[dr, "k_{CT}"'] & M^+(TBC) \arrow[r, "TBC", "k_2"'] & M^+(TBC)_2 \\ & M + TBC^+ & \end{tikzcd} \quad (1)$$

Reanalysis of the earlier results[1] in the framework of the full reaction scheme has given a more satisfactory kinetic picture but does not substantially change the conclusions. The much broader survey of the metallic side of the periodic table described here shows further systematic periodic trends and clarifies the reactivity patterns of TBC with metal ions.

In addition to our work with atomic metal ion complexation with TBC, there have been several recent studies in the FT-ICR ion trap involving association of large, planar, cavity-containing molecules with metal ions. Beauchamp's group reported the complexation of metal ions with porphyrins.[5] The porphyrin molecule $PorH_2$ was found to complex with several metal ions to yield $M(Por)^+ + H_2$. In at least the iron case, association with a second $PorH_2$ molecule was observed to give $Fe(Por)(PorH_2)^+$. Dearden's group has studied cavity-size effects in complexation of metal ions with polyethers and related ligands.[6,7] The radiative association of alkali metal ions with crown ether molecules to

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form ML^+ and ML_2^+ complexes was readily observed. For formation of ML_2^+, the rate showed a strong maximum for the first alkali cation significantly larger than the cavity, the rate being much lower when the metal ion could fit in the cavity. Brodbelt's group used collision-induced dissociation to study cavity-size effects in complexes of small ions with crown ethers, formed by an LSIMS technique.[8] Marshall's group studied electronic effects in the binding of lanthanide ions to tri-*tert*-butylbenzene.[9] Formation of ML^+ and ML_2^+ complexes was observed, with the rate strongly depending on the metal ion. The metal ion effects were understood in terms of electronic effects, specifically the promotion energy of a 4f electron to the 5d level in the metal ion.

Experimental Section

The experiments were performed in the Nicolet Fourier-transform ion cyclotron resonance (FT-ICR) spectrometer.[10] Metal ions were produced by laser desorption–ionization from the solid metal surface, using a pulsed CO_2 laser at powers estimated at 10^9 W cm^{-2}. The metal ions and reaction products were trapped for times up to 30 s and then sampled by FT-ICR detection. TBC reactant molecules were evaporated into the cell from a probe heated to about 120 °C. Reactant neutral pressure was on the order of 1×10^{-8} Torr.

Figure 1 shows the typical evolution of the ion population with time after the laser pulse. Rates of the reactions were determined from the plots of ion abundance versus time, as illustrated in Figure 2. Each point represents a single laser shot, with the sum of ion abundances normalized for each laser shot. The reproducibility of the points was good, and the data shown in Figure 2 are typical in terms of the scatter of the points around smooth plots. All of the reaction rates were standardized against the reaction of Fe^+ with TBC, either by simultaneous observation of the reactions of Fe^+ and the metal ion of interest (as in Figure 1) or by running the Fe^+ reaction directly before and after the reactions of the metal ion of interest. The absolute rate constant for Fe^+ association with TBC was reported in ref 1 to be 6.5×10^{-10} cm^3 molecule^{-1} s^{-1}, with an uncertainty believed to be less than a factor of 2.

The rate constants reported in this work could be determined quite accurately relative to this reference reaction, and the relative comparison of any two rate constants should be accurate to 10%. However, because of the uncertainty in absolute rate constant of the reference reaction, the absolute uncertainties are large, perhaps as large as a factor of 2. This absolute uncertainty also applies to the collisional efficiencies given below in Table II. Some basis for confidence in the absolute values of the rate constants is suggested by the fact that the fastest reaction observed in this study, the reaction of Si^+ with TBC, was found to have a collisional efficiency of 70%, which seems quite reasonable for a very efficient reaction.

Results

For illustration, Figure 1 shows a typical series of spectra at increasing delay times between metal ion production and FT-ICR sampling. The rapid decay of M^+, the buildup of M^+(TBC) and TBC^+, and the subsequent appearance of $M^+(TBC)_2$ are all clear. Figure 2 shows the correspondence of this series of spectra to the kinetic model of eq 1, showing a good fit. This plot yields the Pd^+ rate constants given in Table I.Table I summarizes the rate constants obtained for all the metal ions studied. Also shown in Table I are the rate constants previously reported in ref 1 for the first row transition metals, to which we have added estimates of the rates for the charge-transfer reaction which was ignored in the previous analysis. This table also gives the total efficiency of reaction of the metal ion with TBC, found by dividing the sum of the observed rate constants (association plus charge transfer) by the calculated rate constant (Langevin rate constant) for orbiting ion–neutral collisions.[11]

In the course of working with the heavy metals, some other ions were formed under conditions where reactions with TBC could be observed. While kinetics were not always determined quantitatively, the ready formation, or non formation, of the corresponding complexes is still interesting. Sodium ion was often formed abundantly. It reacted readily to form complexes with one and two TBC ligands,

$$Na^+ \rightarrow Na^+TBC \rightarrow Na^+(TBC)_2 \qquad (2)$$

Potassium formed the K^+TBC complex readily, but no $K^+(TBC)_2$ was found (rate less than 0.1×10^{-10}). Cesium ions were also frequently formed, but they did not react at an appreciable rate with TBC, and no complexes were observed.

Aluminum ion was sometimes formed from the laser striking the probe. Abundant Al^+TBC was observed, but no $Al^+(TBC)_2$ (rate less than 0.05×10^{-10}).

Some of the metals formed oxide ions MO^+, and these ions typically showed ready formation of the MO^+(TBC) adduct. However, addition of a second TBC to these complexes was not observed. Metals for which the MO^+ and MO^+(TBC) species were observed were vanadium, titanium, and molybdenum.

In some runs the background water concentration was significant, and hydration products were observed. For some metals (V, Na, Ti) an ion assigned as $M^+(TBC)(H_2O)$ was observed with substantial intensity, apparently as an association product of M^+(TBC) with background water vapor. For Na and Ti, a further hydration product $M^+(TBC)(H_2O)_2$ was also observed.

Silicon-containing ions appeared to be uniquely reactive with water. For all three silicon-containing ions, water reactions played a major role in the kinetics, and these reactions were included in the computer-fitting procedure. The reaction of Si^+ with water to give $SiOH^+$ was rapid; since the rate constant for this reaction is known (2.3×10^{-10} cm^3 s^{-1}),[12] the background water pressure could be assigned (3×10^{-9} Torr). Then the rate constant could be obtained for the association reaction

$$Si^+(TBC) + H_2O \rightarrow Si^+(TBC)(H_2O) \qquad k = 3 \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \quad (3)$$

$Si^+(TBC)_2(H_2O)$ was also formed, apparently from $Si^+(TBC)_2$ + H_2O, with a similar rate constant. These silicon-containing ions were the only ions in the entire study whose reactions with background water were sufficiently fast that they needed to be included in the kinetic analysis. Under identical conditions, for instance, the reactions of the corresponding iron ion–TBC complexes with water were unmeasurably slow.

Discussion

Formation of Monomer and Dimer Complexes. This work offers indirect evidence about the stability and bonding strengths of the various complexes, because the rate of adduct formation is closely tied to the binding energy of the complex.[13] The formation of a stabilized adduct, either the monomer complex (k_1 reaction) or the dimer complex (k_2 reaction), requires that the initial internal energy of the collision complex be dissipated more rapidly than redissociation into reactants. At the very low pressures of these experiments, collisional stabilization is negligible and only radiative stabilization can lead to complex formation. Stabilization by emission of an infrared photon is expected on a typical time scale of tens of milliseconds.[14] The probability that this will lead to successful complex stabilization depends very strongly on the binding energy. It was estimated in ref 1 that approximately

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[9] Yin, W. W.; Marshall, A. G.; Marcalo, J.; Pires de Matos, A. *Proceedings of the 40th ASMS Conference on Mass Spectrometry*, Washington, D.C., May 31–June 5; 1992; p 1236.

[10] For a description of FT-ICR techniques, see for instance: Dunbar, R. C.; Asamoto, B. In *Analytical Applications of FT-ICR Mass Spectrometry*; Asamoto, B., Ed.; VCH: New York, 1991; Chapter 2.

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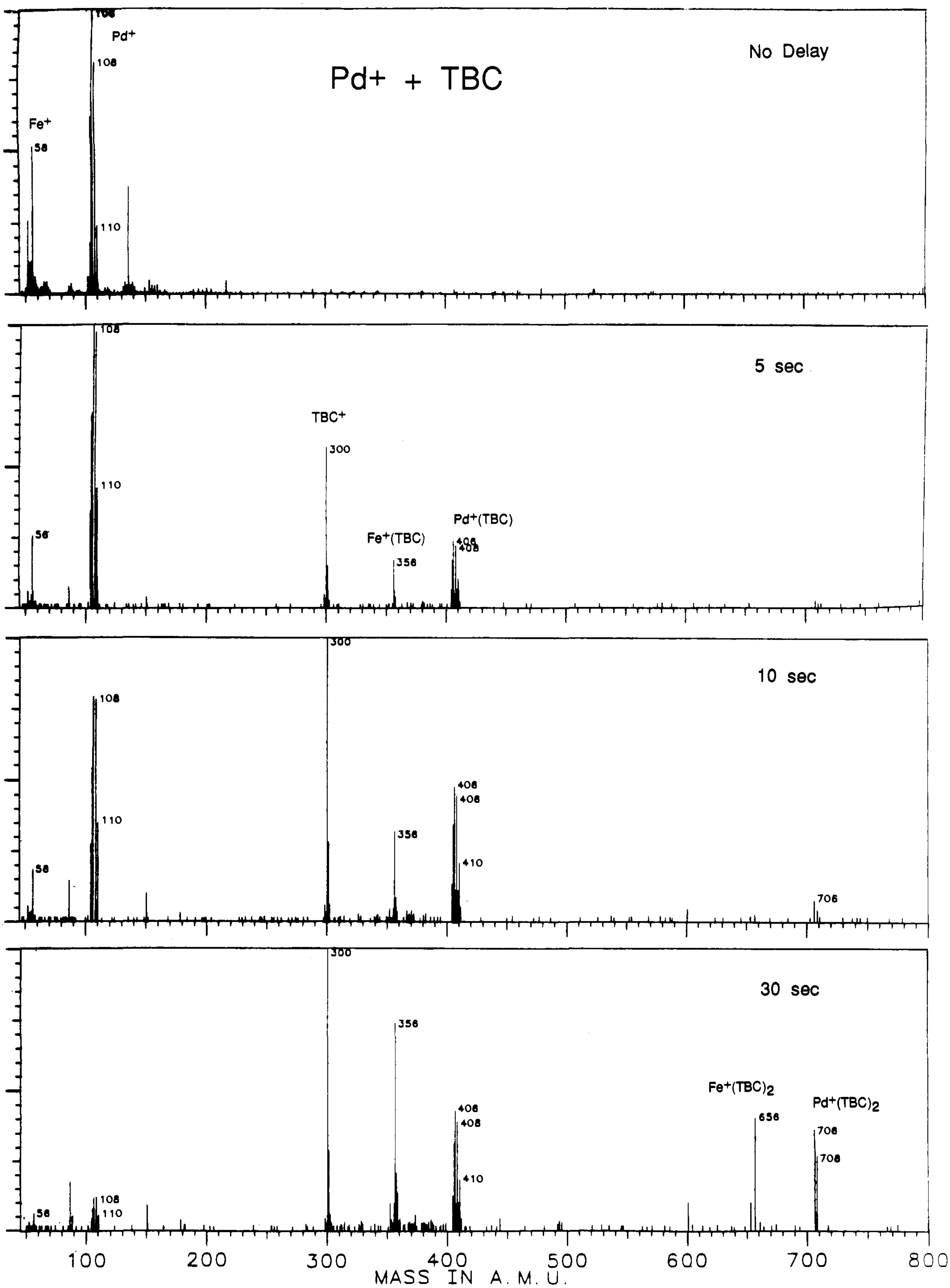

Figure 1. Sequence of spectra for the reactions of Pd^+ with TBC, showing ion abundances at several times following the ionizing laser pulse. Pd isotopes are 105 (23%), 106 (27%), 108 (27%), and 110 (14%). Fe^+ is also created by the laser pulse, and its reactions with TBC (whose rates are already known) provide a convenient internal kinetic standard for calibrating the pressure of neutral TBC.

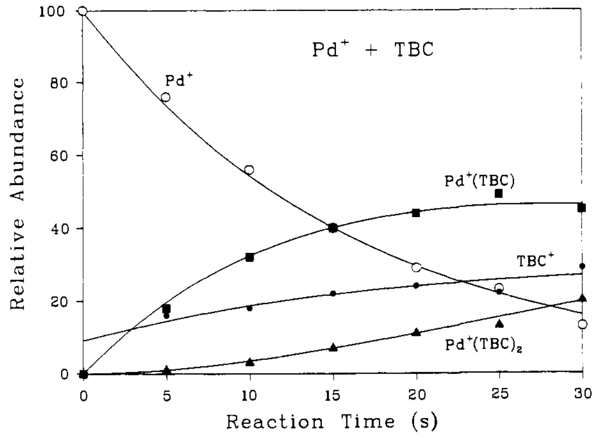

Figure 2. Ion abundance plots for Pd^+ with TBC from spectra like those of Figure 1. The solid lines are fitted theoretical curves for the kinetic mechanism of eq 1, using the rates constants given in Table I.

Table I. Kinetics of Reactions of Metal Cations with TBC

metal ion	k_1[a]	k_2[a]	k_{ct}[a,b]	Eff[c]	IE (eV)[d]
Na	large	0.6	–		5.14
K	large	<0.1	–		4.34
Cs	<0.05		–	<0.01	3.89
Al	large	<0.05	–		5.99
Si	16	2.7	4.4	0.70	8.15
Ti	6.6	2.7	<0.2	0.40	6.82
V	6.0	2.0	<0.2	0.36	6.74
Cr	5.9	2.7	<0.2	0.39	6.76
Mn	5.7	1.3	<0.7	0.33	7.43
Fe	6.6	1.0	1.3	0.42	7.87
Co	6.6	0.3	<0.1	0.33	7.86
Ni	9.0	0.13	<2	0.45	7.64
Cu	4.8	<0.2	10	0.74	7.73
Zn	<0.05		12	0.63	9.39
Mo	1.8	1.6	0.6	0.23	7.10
Rh	2.1	1.4	1.6	0.32	7.46
Pd	2.9	1.2	0.6	0.29	8.34
Ag	3.7	1.5	7	0.76	7.58
Re	1.0	1.4	2.4	0.37	7.76
Pt	1.4	0.7	1.0	0.24	8.61
Au	0.25		3.2	0.27	9.23
Pb	1.1	<0.1	–	0.08	7.41

[a] 10^{-10} cm^3 $molecule^{-1}$ s^{-1}. [b] Numbers showing an upper limit ("<" sign) indicate no significant observed charge-transfer product. Numbers without the "<" sign were observed directly but are still to some extent upper limits, since in most cases there were other minor contaminant ions which may have contributed to the charge-transfer product ion signal at m/z 300. Entries marked "-" indicate that little or no charge transfer was observed, but a quantitative upper limit was not derived. [c] Total reaction efficiency for M^+ reacting with TBC, that is, the sum of k_1 and k_{ct} divided by the calculated orbiting collision rate. [d] Ionization energy of the atom.[20] For reference, the ionization energy of TBC is 7.4 eV.

1.5 eV or more of binding energy would permit efficient radiative stabilization of the monomer complex, and approximately 1.0 eV or more for the case of the dimer complex. These estimates remain valid for the heavier metals considered here. Our interpretation of the k_1 and k_2 values in Table I is that when efficient adduct formation is observed (rate constant on the order of 10^{-10} or greater), this unambiguously signals strong complex binding, exceeding the energy lower limits noted. Failure to observe efficient formation of the complex may in some cases be due to competing charge transfer (zinc and gold, for instance), but otherwise it signals weaker complex binding than these lower limits.

It was found for the first-row transition metal ions, and confirmed for a wider variety of atomic ions in the present work (with cesium ion as the only exception), that formation of the monomer complex (the k_1 process) is efficient unless it is masked by a competing reaction. We generalize to conclude that the solvation of almost any bare atomic ion by a TBC molecule is energetically favorable and gives a binding energy greater than 1.5 eV.

Table II. Collisional Efficiencies for Formation of $M(TBC)^+$ and $M(TBC)_2^+$

metal ion	Eff(1)[a]	Eff(2)[b]
Na	large	0.05
K	large	<0.01
Cs	<0.005	
Al	large	<0.004
Si	0.55	0.23
Ti	0.40	0.23
V	0.36	0.17
Cr	0.39	0.23
Mn	0.33	0.11
Fe	0.35	0.09
Co	0.33	0.027
Ni	0.45	0.011
Cu	0.24	<0.02
Mo	0.18	0.15
Rh	0.18	0.13
Pd	0.24	0.11
Ag	0.26	0.14
Re	0.11	0.14
Pt	0.14	0.07
Pb	0.08	<0.01

[a] Efficiency per collision for formation of $M(TBC)^+$ from M^+ + TBC. [b] Efficiency per collision for formation of $M(TBC)_2^+$ from TBC + $M(TBC)^+$.

The rate of formation of the single TBC complex, k_1, shows a considerable degree of periodic regularity. The first-row metals average around 6×10^{-10} cm^2 $molecule^{-1}$ s^{-1}, the second-row metals are a factor of 2 or 3 lower, and the third-row metals are another factor of 2 lower. (Zn and Au are exceptional because of their high ionization energies, and the consequent interference of the charge-transfer reaction). Some, but not all, of this trend can be attributed to the fact that the orbiting rate constant drops from 22×10^{-10} to 13×10^{-10} cm^2 $molecule^{-1}$ s^{-1} on going from Ti^+ to Pb^+, due to the rising reduced mass of the reacting pair. After discounting this factor, we discern a drop in the k_1 reaction of about a factor of 3 in collisional efficiency in going from the metal ions of smallest to largest atomic number in this study. Giving reasons for this trend would be speculative, but it may be related to the recent suggestion[15] that binding energy drops off with decreasing charge density of the cation.

k_2, the rate of sandwich complex formation, seems to show little systematic variation among the different groups of metals, but it shows drastic and interesting variations between ions which might have been thought to be quite similar. (We speak of the "sandwich" complexes, presuming the ion to occupy a central position, although the actual structures of these complexes, and the location of the atomic ion, are unknown.) The previous discussion of the results for the first-row transition metals considered two lines of explanation for the rapid drop-off of k_2 toward the right-hand side of the first transition metal series: One (electronic effects) was based on the fact that the 18-electron shell around the metal in $M^+(TBC)_2$ is filled at Mn^+, and for metals to the right of this the sandwich complex might be destabilized as a result of excess valence-shell electrons. The second (cavity effect) considered the idea that the small ions at the right of the first transition series can probably fit into the cavity of TBC, which would make them less accessible for binding of the second TBC to form the sandwich complex.

A principle aim of the present extension of the cation–TBC chemistry to more of the periodic table was to clarify the importance of these and other possible factors in controlling complex formation. Both of these ideas still seem viable, and the

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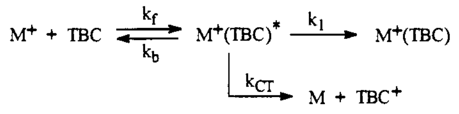
present expanded set of results gives support to a role for both of these effects. All of the second- and third-row transition metals for which k_2 was determined show efficient formation of the sandwich complex. Since they are all too large to fit in the cavity, sandwich complex formation is expected for all of them on the basis of the cavity effect.

In possible support of the importance of electronic bond-formation considerations is the observation that sandwich formation is efficient for most of the second- and third-row transition metal ions measured but is slow or negligible for Cu^+, Pb^+, Al^+, Na^+, and K^+, all of which might well be expected to have poor bond-forming ability.

The Si^+ ion seems unique in several ways. As noted above, it was the only system showing extensive reactions with water: this may reflect the particular affinity of silicon for oxygen.[16] The rate of formation of $Si^+(TBC)$ was the fastest of any ion studied, and its formation appears to occur on more than half the collisions. The rapid formation of sandwich complex for Si^+ is in notable contrast to the behavior of Al^+, which gives a strong argument for the role of electronic effects in governing complexation with TBC. The cavity effect should be similar for these two ions, which should be about the same size. However, in contrast to the filled-shell ^1S ground state of Al^+ (and also Cu^+), Si^+ has a ^2P ground state with a single 3p electron and might be expected to be more reactive and more willing to bind ligands than the former two cases: in a general way this argument would account for its large k_1 and k_2 values. Si^+ is unique in being the only ion in this study having a partially filled p shell, and this could be the basis for its strong complexation behavior. These speculations can only be clarified by a much more extensive survey of the main-group elements than was done in this study.

The alkali metal ions show an interesting trend. Na^+ forms the single TBC complex readily and the sandwich complex somewhat slowly. K^+ forms the single TBC complex readily, but forms no sandwich. Cs^+ shows no complex formation at all. It would appear that going down the series the strength of both first and second complex bonds drops off. The decreasing enthalpy of complexation with increasing alkali ion atomic number is well documented for a variety of smaller ligands, such as, for instance, water,[17] ammonia,[18] and acetonitrile.[17]

The association mechanism can be written



$$\begin{array}{l} M^+ + TBC \underset{k_b}{\overset{k_f}{\rightleftarrows}} M^+(TBC)^* \xrightarrow{k_1} M^+(TBC) \\ \qquad\qquad\qquad\quad \llcorner\xrightarrow{k_{CT}} M + TBC^+ \end{array} \qquad (4)$$

where $M^+(TBC)^*$ represents the unstabilized collision complex. If we take the orbiting collision rate to be the rate k_f at which ion and neutral combine to form collision complexes, then we expect the sum of the rates k_1, k_b, and k_{ct} to equal the orbiting collision rate, which ranges from 31×10^{-10} cm^2 molecule^{-1} s^{-1} for Na^+ to 13×10^{-10} cm^2 molecule^{-1} s^{-1} for Pb^+ (the variation arising from the reduced mass of the reacting pair). Table I shows that $k_1 + k_{ct}$ is nearly always substantially less than the orbiting rate, even for the metals with high ionization energies where charge transfer should dominate over k_b. The quantity Eff given in Table I is the ratio of $(k_1 + k_{ct})$ to the orbiting rate, and it is seen that this reaction efficiency is usually much less than unity. This shows that some orbiting collisions occur in which no intimate complex is formed and which exit back to reactants without either charge transfer or radiative stabilization. The probability of such unproductive collisions appears to be modestly larger for the heavier metals.

Charge Transfer. The charge-transfer reaction has a significant rate (k_{ct}) for some of the metal ions, but in a number of cases where charge transfer is exothermic, it proceeds slowly or not at all. We may ask how it is possible for an association to occur without charge transfer in cases where the ionization energy of the metal is much higher than that of TBC (which is 7.4 eV). In general, the availability of such an exothermic reaction channel is expected to suppress the formation of a stabilized association complex, because the exothermicity of the reaction is released into the collision complex. This accelerates the redissociation (k_b) reaction and also retards radiative relaxation of the complex by greatly increasing the number of IR photons which must be emitted. A good rationalization for the observed successful competition by the radiative association channel comes from considering the effect of the interaction of the approaching metal ion with TBC. The attractive potential energy between metal ion and TBC neutral stabilizes the system according to the interaction potential

$$V(r) = -\frac{e^2\alpha_{TBC}}{2r^4} \qquad (5)$$

where r is the distance between the ion and the neutral and α_{TBC} is the polarizability of the neutral. We have made the extreme simplification of considering the neutral as a spherical, homogeneous ball of polarizable matter, so that this expression and the discussion based on it have conceptual, but not quantitative, value. After the charge transfers to the neutral TBC, the corresponding stabilization potential

$$V'(r) = -\frac{e^2\alpha_M}{2r^4} \qquad (6)$$

where α_M is the polarizability of the metal atom, is much smaller, because the metal atoms are typically much less polarizable than TBC. Within the approximations implied by using the long-range isotropic potentials of eqs 5 and 6, the overall exothermicity of charge transfer at a given separation is

$$\Delta E_{ct}(r) = \Delta IE + (V' - V) = \Delta IE - \frac{e^2(\alpha_M - \alpha_{TBC})}{2r^4} \qquad (7)$$

where $\Delta IE = IE(metal) - 7.4$ eV.

Thus even when charge transfer is exothermic for the separated ion and TBC, it becomes endothermic when the particles approach within a crossover distance

$$r_c = \left[\frac{e^2(\alpha_M - \alpha_{TBC})}{2\Delta IE}\right]^{1/4} \qquad (8)$$

Starting from a tight complex, as the metal separates from TBC, the charge remains on the metal while $r < r_c$. When r_c is crossed, charge transfer becomes exothermic, but if r_c is large, it is likely that the charge will not have time to hop from the metal ion to TBC before the particles separate.

This idea can be illustrated for Pd^+, a case where charge transfer is exothermic by almost 1 eV. When the energies of the Pd^+ + TBC system and the Pd + TBC^+ system are calculated using the interaction potentials of eqs 5 and 6, as shown in Figure 3, it is found that only for distances larger than $r_c = 3.9$ Å is the charge transfer from Pd^+ to TBC exothermic. It is quite reasonable to imagine that charge might not transfer efficiently as the particles separate beyond this fairly large distance. In other words, the transition state for reversion of the energetic complex to reactants may lie inside, or near, the curve crossing, so that the exothermicity of charge transfer is not available to the transition state and is ineffective in speeding up the redissociation. In the language of curve crossing, the separating particles may not follow the adiabatic potential to infinity but may separate diabatically on the curve which correlates to Pd^+ + TBC. This rationalizes the observed fact that many collisions of Pd^+ with TBC result in

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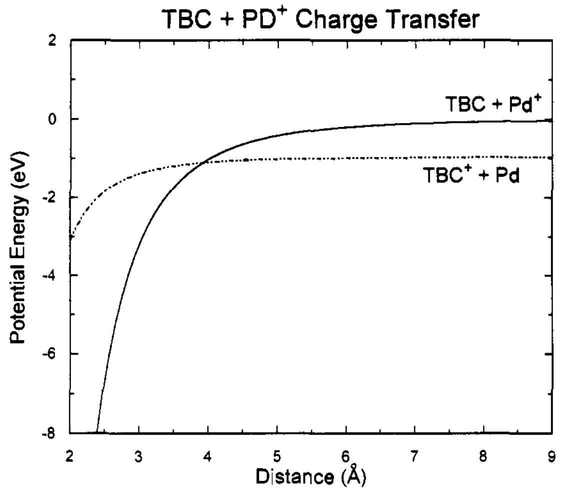

Figure 3. Figure 3. Ion-induced dipole interaction energies for the palladium/TBC system. These are plotted from the spherical long-range potentials of eqs 5 and 6 and do not take into account any short-range or anisotropic interactions. The charge-transfer crossover point is seen to lie at 3.9 Å.

neither complex formation nor charge transfer but separate back into reactants along the asymptotically higher potential curve. Again it should be stressed that quantitatively this picture is no more than a conceptual aid, since the actual interaction between these particles is highly anisotropic and not at all well represented by eqs 5 and 6.

It is possible, and in fact likely, that a fraction of the atomic ion reactants are in excited electronic states.[19] This might have an effect on the observed k_1 and k_{ct} values for M^+ in Table I but seems unlikely to affect the overall observed patterns of high reaction efficiencies for nearly all atomic ions and charge-transfer probabilities correlating sensibly with the relative ionization energies. It seems reasonable to expect that electronic excitation would be quenched in forming ML^+ and that vibrational excitation of the ML^+ reactants would be rapidly dissipated by radiative cooling, so that the ML^+ reactivity patterns probably reflect essentially ground-state reactants.

Conclusions

Nearly all the atomic ions studied associate with TBC with good collisional efficiency to form the ML^+ complex. This reflects the generally strong solvating interaction between the bare atomic ion and the macrocyclic ligand. The high efficiency of the association reaction indicates a binding energy greater than about 1.5 eV (35 kcal/mol). This solvation reaction is suppressed when the competing charge transfer is highly exothermic but is otherwise universal except for Cs^+. The collisional efficiency of this solvation reaction drops modestly in going from lighter to heavier rows of the periodic table.

Association of $M(TBC)^+$ with a second TBC molecule is quite efficient (collisional efficiency in the vicinity of 10–20%) for most of the ions and shows no obvious systematic trend going down the periodic table. However, it drops to low efficiency for several interesting cases. For the late-first-row transition metals (Co, Ni, Cu), it seems most likely that the ion can fit in the central cavity of TBC. When the metal ion is in the TBC cavity, there is apparently no favorable site on the $M(TBC)^+$ complex for interaction with the second TBC ligand, and a sandwich complex is not formed easily. This cavity effect is apparently similar to that seen by Dearden et al.[6] for alkali ions binding to crown ethers. Several other ions (K^+, Al^+, Pb^+) also do not form sandwich complexes efficiently, if at all. Since cavity insertion is an unlikely explanation for these cases, it appears that their unwillingness to add a second ligand reflects poor electronic interaction with the TBC ring, giving a binding energy less than about 1 eV (23 kcal/mol).

The high reactivity of Si^+ to form both the monomeric complex and the sandwich complex is noteworthy and contrasts with the failure of Al^+ to form the sandwich complex. Silicon could be a promising element for condensed-phase complexation with TBC.

Charge transfer from the metal to the ligand is a possible reaction competing with association for many of the ions. However, this reaction predominates only when it is very exothermic (>2 eV). A long-range curve crossing argument, based on the large polarizability difference between metal and ligand, gives a qualitative explanation of this effect.

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(19) See, for instance: Strobel, F.; Ridge, D. P. *J. Phys. Chem.* **1989**, *93*, 5635. Armentrout, P. B. In *Gas Phase Inorganic Chemistry*; Russell, D. H., Ed.; Plenum Press: New York, 1989; pp 1–42. Oriedo, J. V. B.; Russell, D. H. *J. Phys. Chem.* **1992**, *96*, 5314.

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