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Complexation of transition metal ions M^+ ($M = Fe, Co, Ni, Cu, Zn, Ag$) by [2.*n*]paracyclophane-enes ($n = 3, 4, 5, 6$) in the gas phase: effect of the molecular cavity on the complexation capability

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Abstract

Complex formation in the gas phase between transition metal ions $M^+ = Fe^+$, Co^+, Ni^+, Cu^+, Zn^+, and Ag^+ and dimethyl[2.*n*]paracyclophane-enes **1**–**4** ($n = 3$–6) has been studied by secondary ionization mass spectrometry (SIMS) and tandem mass spectrometry. With the exception of Zn^+, complex formation was observed if dry mixtures of salts of a transition metal and a cyclophane were bombarded with a 30 keV primary Cs^+ ion beam in a SIMS ion source. Using liquid SIMS, abundant signals of a complex $[M(cyclophane)]^+$ were only obtained for Ag^+ and NBA as liquid matrix. Besides a large signal of M^+ and a significant signal of $[M(cyclophane)]^+$ all SIMS mass spectra contained a distinct peak of the molecular ion $[cyclophane]^{\cdot +}$ and a series of small peaks of hydrocarbon fragment ions. Dimeric adduct ions $[M(cyclophane)_2]^+$, typical of gas phase complexation of transition metal ions and planar aromatic hydrocarbons, are only detected in the mass spectra of mixtures of **1** and salts of Co or Ag. It is concluded from the experimental results that complex formation occurs in the gas phase of the SIMS ion source by ion/molecule reaction between the sputtered metal ion M^+ and the neutral cyclophane evaporating from the heated target holder in competition with charge transfer. By this model the efficiency of complex formation between a certain metal ion and cyclophane can be estimated from the intensity ratio $r = [M(cyclophane)]^+/[cyclophane]^{\cdot +}$. From this ratio and the results of separate experiments, in which two M^+ compete in complex formation with cyclophane **3** or in which a mixture of cyclophanes is used for complexation of Ag^+, it is shown that complex formation increases in the series $Fe^+ < Co^+ \approx Ni^+ < Cu^+ \ll Ag^+$ and in the series $\mathbf{1} < \mathbf{2} < \mathbf{3} \approx \mathbf{4}$. The selectivity in the series of cyclophanes as well as the lack of formation of dimeric complexes $[M(cyclophane)_2]^+$ concurs with the formation of "in" complexes (**IC**) or "side-on" complexes (**SC**), in which the metal ion is more or less buried in the cavity of the cyclophane ligand. This is corroborated by collision-induced dissociation experiments, which show—with the exception of Ag^+ complexes—intense losses of small hydrocarbon fragments and/or extensive decomposition of the complex ions, but no major dissociation into the components, and by semiempirical AM1 analysis of the structures of the complexes. (Int J Mass Spectrom 210/211 (2001) 311–325) © 2001 Elsevier Science B.V.

Keywords: Cyclophanes; Transition metal ion; Host–guest complex; SIMS; CID

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Dedicated to Professor N. M. M. Nibbering to honor his eminent contribution to organic mass spectrometry.

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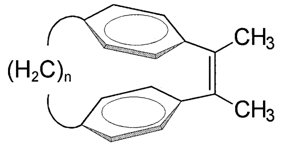
1. Introduction

With expanding research in the field of molecular recognition the study of interactions between guest and host molecules in the gas phase has gained considerable interest [1]. In particular, the binding of metal ions in the gas phase by organic ligands has been studied much in detail. One interesting example is the complexation of alkali ions by crown ethers and related host molecules, which has been investigated using a multitude of mass spectrometric and theoretical methods [2]. Besides binding of cations by lone pairs of suitable heteroatoms of the organic ligands, cation–aromatic π interactions have been suggested as playing an important role in the molecular recognition of many biological and macromolecular systems [3]. Hence, in particular the interaction of transition metal ions in the gas phase with aromatic molecules has been studied by many research groups. An early report is the "cationization" of substituted benzenes and polycyclic aromatic hydrocarbons (PAHs) with Cu^+ or Ag^+ by Cooks and co-workers using secondary ionization mass spectrometry (SIMS) [4]. If transition metal ions M^+ react with benzene and PAH in the gas phase, usually a mixture of monomer ions $[(PAH)M^+]$ and dimer ions $[(PAH)_2M^+]$ is formed. The bond dissociation energy (BDE) for first row transition metal ions of complexes $[(C_6H_6)_xM^+]$, $x = 1,2$ and M = Ti–Cu have been determined by energy resolved collision induced decomposition in a guided ion beam apparatus by Armentrout and co-workers [5], and compared with theoretical calculations by Bauschlicher et al. [6]. These latter authors predicted the bonding to be predominantly electrostatic with a significant enhancement arising from 3*d* backdonation into the π^* orbitals of benzene. The experimental bond energies of one C_6H_6 molecule to M^+ are nonmonotonic across the transition metal row, and the decrease in BDE in going from $(C_6H_6)Ti^+$ to $(C_6H_6)V^+$ to $(C_6H_6)Cr^+$ (with three, four, and five 3*d* electrons) as well as from $Co(C_6H_6)^+$ to $Ni(C_6H_6)^+$ to $Cu(C_6H_6)^+$ has been explained by filling of the energetically unfavorable $3de_1(\pi)$ orbitals, which increases the repulsion with the benzene ligand. Another underlying effect is seen in the decreasing size of the metal ion as one moves to heavier elements, which should increase the electrostatic bonding by allowing shorter metal–ligand distances. In contrast to the BDE of $[(C_6H_6)M^+]$, the BDE for loss of one ligand from $[(C_6H_6)_2M^+]$ show a relatively moderate monotonic decrease across the transition metal row. Consequently, trends in dissociation by loss of two benzenes from $M(C_6H_6)_2^+$ parallel those found for the monobenzene species. Recent theoretical studies have confirmed that electrostatic interactions play a prominent role in cation–aromatic π interactions [7,8]. Besides the electronic configuration and the size of the transition metal ion, the binding of a metal cation is also influenced by the structure of the PAH. Relative Ag^+ ion affinities of some PAH were measured by observing the unimolecular dissociation of asymmetric Ag^+ bound dimers and using the kinetic method [9]. The dissociation of the mixed complexes proceeds mainly by formation of the monomeric Ag^+–arene complexes with only minor amounts of loss of neutral AgH. The relative Ag^+ affinities (relative to benzene) correlate moderately with theoretically calculated quadrupole moments of the PAH, showing that the binding of Ag^+ is also mainly electrostatic in nature. However, secondary effects are observed which are explained inter alia by steric hindrance of the complexation of Ag^+. A particularly interesting effect of the structure of aromatic compounds on their ability for complexation of metal cations has been observed by Pozniak and Dunbar by comparing the gas phase complexation of coronene and tribenzocyclyne [10]. All transition metal ions readily form dimer sandwich complexes with coronene, but for the smaller ions Ni^+ and Cu^+ no dimer formation is observed with tribenzocyclyne. This was attributed to a "cavity effect" inasmuch as the small metal ions can penetrate into the central cavity of the tribenzocyclyne ligand, thus obstructing the attachment of a second ligand for formation of a sandwich complex. A recent theoretical study of the binding of metal ions to several organic π ligands confirmed this cavity effect [11]. This observation indicates that complex formation between transition metal ions and quite simple π molecules can exhibit selectivity. Cyclophanes are bridged aromatic molecules having



n	
3	**1**
4	**2**
5	**3**
6	4

Scheme 1.

a molecular cavity the size of which depends on the nature of the bridges between the two benzene rings. In connection with studies about the potentialities of the McMurry coupling reaction for the synthesis of cyclophanes we had synthesized a series of dimethyl[2.*n*]paracyclophan-enes **1**–**4** (see Scheme 1) with $n = 3$–6 [12]. These cyclophanes contain an etheno bridge and an oligomethylene chain as the second bridge at the two para-phenylene groups. Accordingly, these molecules can be viewed as "[*n*]parastilbenophanes" in which a cis-stilbene unit is bent by the oligomethylene chain spanning the para positions. The molecular cavity of these cyclophanes is formed by the two benzene rings, which are kept more or less in a face-to-face position, the etheno bridge, and the oligomethylene chain, and the size of the cavity as well as the opening angle between the two benzene rings depends on the number *n* of the CH_2 groups. It appeared feasible that these molecules should exhibit a selectivity for a complexation of transition metal ions depending on the details of the possible conformations of the cyclophanes **1**–**4** and the size and favored ligand orientation of the metal ion. The cyclophanes are nonpolar hydrocarbons which do not dissolve in the solvents used for electrospray ionization. Therefore, we have investigated the gas phase complexation of the first row transition metal ions Fe^+, Co^+, Ni^+, Cu^+, and Zn^+ as well as Ag^+ with **1**–**4** using the SIMS method. The results show that these metal ions with the exception of Zn form readily monomeric complexes in the gas phase with **1**–**4** of the type $[M(cyclophane)]^+$, whereas dimeric complexes $[M(cyclophane)_2]^+$ are found only in the case of **1**. Complex formation is especially abundant for cyclophanes with a larger molecular cavity, but with respect to the nature of the metal ion only a moderate selectivity is observed, however.

2. Experimental

The synthesis of the dimethyl[2.*n*]paracyclophan-enes **1**–**4** was described previously [12]. The transition metal salts used in this study are commercially available and were used without further purification.

Mass spectrometry: All mass spectrometric measurements were performed with a double focusing mass spectrometer VG AutoSpec equipped with a 30 keV Cs^+ liquid SIMS ion source [13]. The mass spectra were obtained at an accelerating voltage of 8 keV and a mass resolution of $m/\Delta m = 2600$. Collision induced decomposition (CID) of ions was achieved by focusing the selected ions into the collision cell of the third field free region after the magnetic sector field of the AutoSpec mass spectrometer and introducing argon as the collision gas into the cell until the intensity of the main ion beam was reduced to about 60%. The resulting CID mass spectra were obtained by scanning the voltage of the second electrostatic analyzer following the magnetic field.

Initially it was tried to generate adduct ions from the cyclophanes **1**–**4** and metal ions using the typical conditions of liquid SIMS by dissolving or dispersing the respective cyclophane and transition metal salt in a suitable liquid matrix [glycerol, triethylene glycol, 2,4-tert.amylphenol, *m*-nitrobenzylalcohol (NBA)] and bombarding the solution with the primary 30 eV Cs^+ ion beam in the liquid SIMS ion source. By this procedure only adduct ions of **1**–**4** and Ag^+ or Cu^+ could be detected if NBA is used as the liquid matrix. It was noted for salts of the other transition metals, however, that weak signals of the adduct ions appeared at the end of the experiment after most or all of the liquid matrix had been evaporated from the target holder in the ion source. This observation directed us to develop the following SIMS procedure for a reliable generation of adduct ions from metal salts and cyclophanes.

An amount of the transition metal salt about equimolar to the cyclophane was carefully suspended or dissolved in a droplet of distilled water of about 5 μL which had been deposited on the metal target holder of the liquid SIMS ion source. Then, about 1

Table 1
Relative ion intensities (% of total ion current) in SIMS spectra of mixtures transition metal salt/[2.n]paracyclophan-ene (C)

	$FeCl_3$/cyclophane				$CoCl_2$/cyclophane				$NiCl_2$/cyclophane				Cu(ac)$_2$/cylophane				Ag(tfl)/cyclophane[a]			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
$\mathbf{M(C)}_2$	...	...	...	...	1.0	...	...	...	...	...	...	...	...	...	...	...	1.8	...	...	...
$(\mathbf{MC})^+$	1.7	1.2	2.4	0.5	6.9	10.6	7.3	5.0	3.1	5.2	3.0	2.7	20.8	36.4	8.0	36.3	30.4	58.5	43.2	46.3
$\mathbf{C}^{\cdot+}$	3.5	1.7	2.9	1.5	1.0	0.9	0.9	0.2	3.3	2.0	1.2	8.4	4.9	0.9	1.1	0.3	24.5	23.7	12.8	15.4
$C_{18}H_{17}^+$	2.2	1.4	1.5	...	...	...	...	...	...	1.3	1.5	...	...	2.7	...	...				
$C_{17}H_{15}^+$	...	2.7	3.2	1.3	...	1.6	1.1	0.6	...	3.6	2.2	3.5	...	4.7	1.2	...				
$C_{16}H_{10}^+$	2.7	2.5	4.1	1.2	2.1	1.7	1.5	0.5	3.6	4.4	...	3.9	1.9	1.5	...	...				
$C_{15}H_9^+$	2.4	1.9	2.9	1.0	2.1	1.5	1.4	0.4	3.1	4.3	1.8	2.2	1.6	1.3	3.5	0.4				
$C_{14}H_{10}^+$	1.5	1.4	3.0	0.7	...	1.2	0.9	0.2	3.0	3.0	...	...	...	...	...					
$C_{13}H_9^+$	2.3	2.1	3.8	0.8	1.7	1.8	1.5	0.5	4.3	4.3	3.9	4.2	1.5	1.2	3.4	...				
$C_{12}H_8^+$	1.7	1.6	3.1	0.8	1.2	1.7	1.0	0.4	3.1	3.0	2.1	2.1	0.7	...	3.4	...				
$C_{11}H_9^+$	1.7	1.5	3.5	0.8	...	1.2	1.1	0.3	3.3	3.8	2.7	3.0	0.6	0.7	...	0.5				
$C_{10}H_8^+$	3.5	3.1	6.1	1.6	2.7	2.3	2.3	0.8	5.5	6.2	5.1	6.3	2.3	1.9	1.7	0.5				
$C_7H_7^+$	3.9	4.6	7.2	5.6	2.9	2.8	2.0	0.7	16.5	8.2	12.2	11.5	4.3	4.2	6.5	0.6				
M^+	63	68	41	80	71	65	74	89	29	25	29	23	49	40	60	60	43	18	44	38
r^2	0.5	0.7	0.8	0.3	6.9	11.8	8.1	16.7	0.9	2.6	2.5	0.3	4.2	40.4	7.3	121	1.2	2.5	3.4	3.0

[a] Mass spectrum obtained by liquid SIMS and NBA as matrix.
[b] $r = [\mathbf{MC}^{\cdot+}]/[\mathbf{C}^{\cdot+}]$.

mg of the powdered cyclophane was put on top of the droplet. The target holder carrying the mixture was introduced into the vacuum lock of the ion source, and the water was evaporated slowly before introducing the target holder into the ion source. The metal salts used were $FeCl_3$ or Fe(acac)$_3$, $CoCl_2$, $NiCl_2$, or $NiBr_2(H_2O)_3$, $CuCl_2$ or Cu(ac$_2$)$_2$, $ZnCl_2$ or Zn(ac$_2$)$_2$, and $AgCF_3SO_3$ or $AgCF_3CO_2$, but the result did not depend significantly on the specific anion of the salt used. Before starting each measurement the Cs^+ ion gun was conditioned by heating for about 30 min at an accelerating voltage of 10 keV. At the start of the measurement the accelerating voltage of the Cs^+ gun was increased to 30 keV and the heating of the Cs reservoir was increased until an intense primary ion beam of Cs^+ was obtained. After a short induction period the mass spectrum of the secondary ions generated from the mixture on the target holder became constant for 10 min or more. All spectra shown were obtained by an accumulation of at least ten single spectra.

The procedure used is essentially a SIMS method and is similar to the method used by Cooks and co-workers with the exception that the latter authors generated the metal ions by sputtering from metal foils [4]. The peak of the respective metal ion of the salt used was always by far the most intense signal of the mass spectrum. In addition, some Cs^+ originating from backscattering of the primary ion beam were also observed. The intensity distribution of the secondary ions was reproducible within ±10% relative intensity if the same sample preparation was used for several experiments. By preparing a new sample the intensity variation of the peaks of the mass spectra was somewhat greater. However, in particular, the intensity ratio of the molecular ion of the cyclophane and the adduct ion did not vary much for samples of the same mixture of a metal salt and a cyclophane.

3. Results and discussion

The mass spectra obtained from mixtures of cyclophanes **1**–**4** and salts of the transition metals M = Co, Fe, Ni, and Cu are presented in Table 1, and Fig. 1 displays some spectra of mixtures of the salts of the transition metals with a cyclophane to give a visual impression of these mass spectra. In the SIMS spectra of mixtures of salts of Zn^{2+} and **1**–**4** no adduct ions

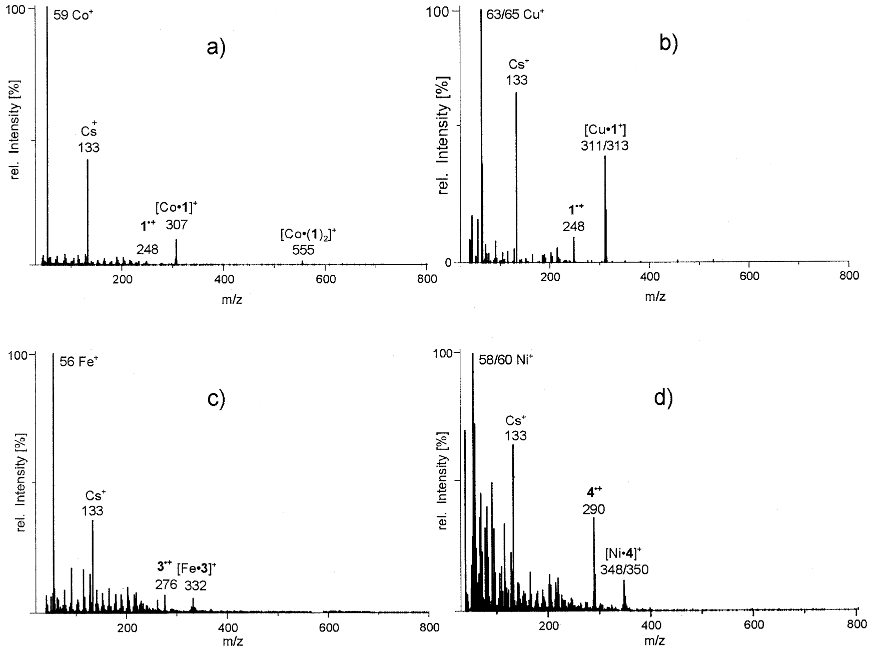


Fig. 1. SIMS mass spectra of mixtures of (a) $CoCl_2$/**1**, (b) $Cu(ac)_2$/**1**, (c) $FeCl_3$/**3**, and (d) $NiCl_2$/**4**.

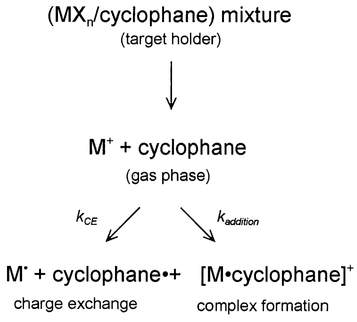
$[Zn(cyclophane)]^+$ or $[Zn(cyclophane)_2]^+$ were observed. Instead, very weak signals appeared which could be attributed to ions $[ZnCl(cyclophane)]^+$, but this was not further explored. The formation of complexes of Ag^+ with **1**–**4** was measured using liquid SIMS (NBA as matrix). These latter spectra contain a multitude of peaks that originate from NBA or complexes of Ag^+ with NBA. However, the signals due to Ag^+, to the molecular ions of the cyclophane, and to the complex ions $[Ag(cyclophane)]^+$ are usually the most intense signals, and only their intensities are given in Table 1. Besides $AgCF_3SO_3$ or $AgCF_3CO_2$, mixtures of salts of the other transition metals used and cyclophanes **1**–**4** did not give meaningful liquid SIMS spectra. The reason for this is very likely that neither the cyclophanes nor the salts dissolve in most of the liquid matrices besides NBA. Further, the polar molecules and fragments of the NBA matrix compete effectively with the cyclophanes for complex formation with the metal ion. The ion Ag^+ is obviously an exception because its well known affinity towards aromatic compounds. In the spectra obtained by SIMS without a liquid matrix, the peak of the metal ion M^+ is always by far the most intense signal of the spectrum, together with a signal of varying intensity of ions Cs^+, *m/z* 133, which obviously originate from backscattering of the primary Cs^+ ion beam. This latter peak is not included in Table 1. Further significant peaks observed in these spectra arise from the monomeric adduct ion $[M(cyclophane)]^+$ and from the molecular ion of the cyclophane. The lower mass range of the spectra is crowded with small peaks presumably coming from the background, but peaks due to fragment ions arising from the ionized cyclophanes can be also identified. The most intense ones correspond usually to ions $C_{16}H_{10}^+$, *m/z* 202 and $C_7H_7^+$, *m/z* 91. The formation of these fragment ions requires considerable rearrangement and fragmentation of the cyclophane structure [14], but some ions may also originate from radiation damage of the neutral cyclophane by the primary ion beam. A signal of the dimeric adduct ion $[M(cyclophane)_2]^+$ is only observed in the spectrum of the mixture of cyclophane **1** with Ag and Co salts. However, no intense spectra could be obtained by SIMS from mixtures of Fe salts and cyclophane **1**, so that a weak signal due to the dimeric adduct may have escaped detection in this case.

Table 2
Ionization energies (IEs), radius of atom (r_{atom}), radius of ion (r_{ion}), covalent radius (r_{cov}), and cordination radius (r_{coord}) of transition metals

Transition metal	IE[a] (eV)	r_{atom}[a] (pm)	r_{ion} (charge)[a] (pm)	r_{cov}[a] (pm)	r_{coord}[b] (pm)
Fe	7.87	172	74 (2+)	117	183
Co	7.86	167	72 (2+)	116	185
Ni	7.835	162	69 (2+)	115	175
Cu	7.726	157	72 (2+) 96 (1+)	117	186
Zn	9.934	153	74 (2+) 88 (1+)	125	. . .
Ag	7.576	175	89 (2+) 126 (1+)	134	235

[a] Taken from [16].
[b] Taken from [10].

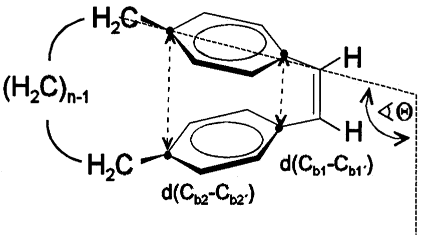
It is clear from the experimental setup and the behavior of the mixtures of the salts of transition metals and cyclophanes **1–4** during the SIMS measurements that the adduct ions observed in these mass spectra are not preformed ions within the mixture which are sputtered by the primary Cs^+ ion beam. Only in the case of the of the liquid SIMS of Ag^+/cyclophane mixtures in NBA preformed adduct ions could have been observed. In all other cases we suggest that the adduct ions are formed by chemical ionization in a vapor plume in the SIMS ion source above the target holder. This is corroborated by the observation that in the initial period of the SIMS experiment only abundant transition metal ions are observed in the spectra, whereas the evolution of signals of the adduct ions and the molecule ions of the cyclophane is delayed and becomes steady only after some minutes. This behavior indicates direct sputtering of the transition metal cation (and reduction to the monovalent cation M^+ probably by the organic material present) whereas most of the solid cyclophane is evaporated as neutral molecules from the metallic target holder if its temperature rises with time because of the bombardment with Cs^+ ions. At this time, the metal ions M^+ pervade a cloud of neutral molecules of the cyclophane and undergo ion/molecule reactions. The ionization energies (IES) of the respective transition metals are shown in Table 2. The IE of cyclophanes **1–4** are unknown, but the IEs of some related cyclophanes are known, and range from 7.8 eV for [2.3]paracyclophane to 8.1 eV for [2.2]paracyclophane and [2.2]paracyclophane-diene [15]. From these data an IE of 7.8 ± 0.2 eV is estimated for **1–4**. This is close to the range of IE of the transition metals used in this study [IE(Ag) = 7.576 eV to IE(Fe) = 7.870 eV] with the exception of Zn, which exhibits a significant greater IE of 9.394 eV [16]. From the IE data it is plausible, that one of the ion/molecule reactions occurring in the vapor plume above the target holder is charge exchange between the metal ion and the cyclophane, in particular if one takes into account kinetic energy of the sputtered metal ions. In this connection one should note that the spectra obtained by SIMS from mixtures of the Zn salts and cyclophanes display no peaks of the adduct ions, but major peaks of the molecular ions of **1–4**. Obviously, because of the large IE(Zn), charge exchange with the cyclophane is the only substantial ion/molecule reaction of Zn^+. For Fe^+, Co^+, Ni^+, and Cu^+ as sputtered metal ions, a second ion/molecule reaction is evidently the addition of the metal ion to the cyclophane (Scheme 2). The conditions in the vapor phase in front of a target holder in the high vacuum of the SIMS ion source are not well defined. Certainly the number density of cyclophane molecules decreases quickly with the distance from the surface of the target holder. Thus, the chance for secondary reactions of the metal ion traveling through the cloud and for the formation of dimeric adduct ions $[M(\text{cyclophane})_2]^+$ is small. Nonetheless, the forma-



Scheme 2.

Table 3
Molecular geometry parameters of structures of cyclophanes **1***–**4*** calculated by AMI

Cyclophane	d (C_{b1}–C_{b1}) (pm)	d (C_{b2}–C_{b2}) (pm)	$\sphericalangle\Theta$ (deg)
1*	274.6	321.5	103
2*	278.9	391.7	108
3*	280.2	451.0	110
4*	285.1	487.4	114.5



Scheme 4.

tion of dimeric [M(cyclophane)$_2$]$^+$ is unambiguously observed, but only from mixtures of Ag and Co salts with **1**. Thus, principally a cyclophane can form a dimeric adduct with transition metal cations as other PAH do, and this process is definitely observed under the present experimental conditions. However, formation of dimeric adduct ions depends clearly on the nature of the transition metal ion and the cyclophane. If one considers the radii of the relevant metal atoms and ions (Table 2) and compares these with the size of the molecular cavity of the cyclophanes (see Table 3), it is significant that under the present conditions dimeric adduct formation is only observed for the biggest metal cations Ag$^+$ and Co$^+$ and the cyclophane **1** with the smallest cavity. Evidently, steric effects inhibit formation of the dimeric adducts in the other cases, and this steric affect may be indeed the cavity effect introduced by Dunbar and co-worker [10] and Klippenstein and Yang [11].

From the experimental conditions and the intensity and the appearance of the resulting mass spectra it is inferred that the ability of complex formation increases from Fe$^+$ and Ni$^+$ to Cu$^+$ and Ag$^+$, and that complex formation is distinctly more pronounced for cyclophanes **3** and **4** than for **2** and in particular for **1**. The distinct affinity of Cu$^+$ and especially of Ag$^+$ to aromatic molecules is know from previous studies [4,5,10]. According to our suggestion complex formation occurs in competition with charge transfer between the metal ion M$^+$ and the cyclophane under the experimental conditions used (Scheme 2). In this case the ratio r of the peak intensity of the adducts ion [M(cyclophane)]$^+$, [$\mathbf{MC}^+$], and the intensity of molecular ion of the cyclophane, [$\mathbf{C}^{\cdot+}$], corresponds to the ratio of the rate constants $k_{\text{add}}/k_{\text{CE}}$ of the competing ion/molecule reactions. The IEs of Fe, Co, Ni, and Cu are not very different; similarly the IEs of **1**–**4** are almost identical. Thus, the rate constants of the charge transfer from the metal ions to the cyclophanes are not very different, since all mass spectra were measured under the same conditions. Then, by this simple reaction model, the variation of the intensity ratio [$\mathbf{MC}^+$]/[$\mathbf{C}^{\cdot+}$] reflects mainly the variation of the rate constant of complex formation. The values of r = [$\mathbf{MC}^+$]/[$\mathbf{C}^{\cdot+}$] from the SIMS experiments are shown in the last row of Table 1. The data exhibit substantial scattering, as expected from the oversimplified model, but by this semiquantitative criterion Cu$^+$ is again clearly the metal ion of highest ability of complex formation with all cyclophanes, whereas Fe$^+$ is the least reactive ion. With respect to the reactivity of the cyclophanes in metal ion complexation, **1** with a small molecular cavity behaves always as a rather bad host for the transition metal ions. It is possible that **4** with the largest cavity is also less reactive than **2** and **3**, in particular if the intensity of $\mathbf{MC}^+$ in the spectra is also considered (Table 1), but this effect is not very clear due to the scattering of the data.

The get a more direct information about the ranking of the cyclophanes **1**–**3** in complex formation, an equimolar mixture of the three cyclophanes and excess $AgCF_3SO_3$ in NBA was analyzed by liquid SIMS. The resulting mass spectrum shown in Fig. 2(a) reveals that **1** is indeed the least effective host molecule for Ag$^+$, and that **3** is more efficient by a factor of about 4 in generating complexes with Ag$^+$.

Additional experiments have been performed, in which two metal cations compete for the same host, to get information about the ability of the different transition metal ions to form complexes with a certain cyclophane. Accordingly a series of equimolar mixtures of two salts of different transition metals Fe, Co,

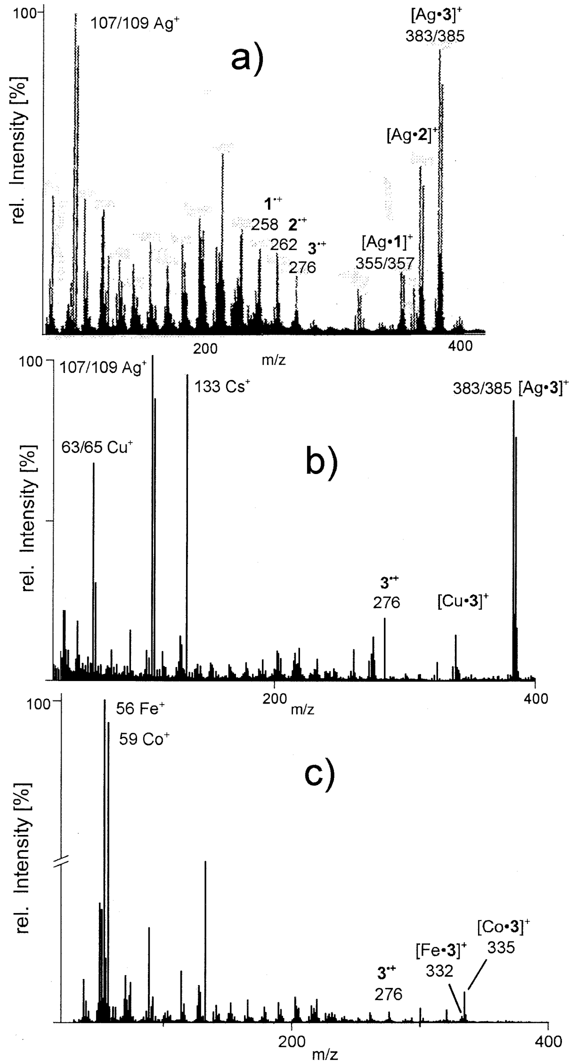
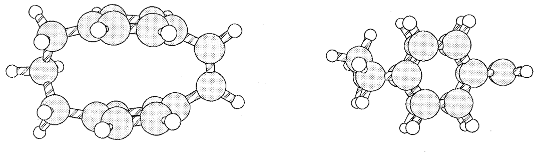


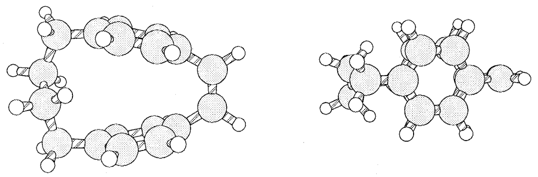
Fig. 2. SIMS mass spectra of mixtures of (a) Ag(tfl)/**1**/**2**/**3**, (NBA matrix), (b) Cu(ac)$_2$/Ag(tfl)/**3**, and (c) FeCl$_3$/CoCl$_2$/**3**.

Ni, Cu, or Ag, and adding cyclophane **3** as a host molecule was examined by SIMS, since cyclophane **3** is an adequate host for all transition metal cations. Two examples for the spectra obtained are shown in Fig. 2(b) and (c). To correct for the different concentration of the sputtered metal ion M_1^+ and M_2^+, the ratio of the intensities $[M_1 \cdot \mathbf{3}]^+/[M_1^+]$ and $[M_2 \cdot \mathbf{3}]^+/[M_2^+]$, respectively, in the same mass spectrum is compared as a semiquantitative measure of the relative capability of complex formation $C_{\mathrm{rel}}(\mathbf{3}) = ([M_1 \cdot \mathbf{3}]^+/[M_1^+])/([M_1 \cdot \mathbf{3}]^+/[M_1^+])$ for cyclophane **3**. The following $C_{\mathrm{rel}}(\mathbf{3})$ were obtained: $\mathrm{Fe^+/Co^+} = 1/8$; $\mathrm{Fe^+/Ni^+} = 1/5$; $\mathrm{Fe^+/Cu^+} = 1/24$; $\mathrm{Co^+/Ni^+} = 1/2$; $\mathrm{Co^+/Cu^+} = 1/6$; $\mathrm{Ni^+/Cu^+} = 1/4$; and $\mathrm{Ag^+/Cu^+} = 4/1$. This shows again the order $\mathrm{Fe^+} < \mathrm{Co^+} \approx \mathrm{Ni^+} < \mathrm{Cu^+} < \mathrm{Ag^+}$ for the ability of these transition metal ions to generate adducts with the [2.*n*]paracyclophanes.

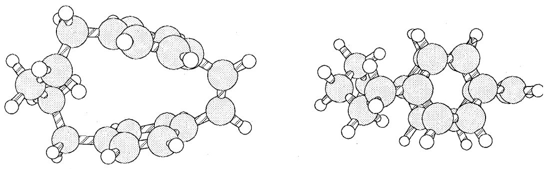
A detailed characterization of the adduct ions formed from transition metal ions and cyclophanes **1**–**4** by advanced ab initio methods is out of reach of the present experimentally oriented study and must await further investigation. However, to get an impression of the structure and relative energy of formation of the complex ions, the structures and conformations of the para-[2.*n*]cyclophanes and their complexes with the transition metal ions $\mathrm{Fe^+}$, $\mathrm{Co^+}$, and $\mathrm{Ni^+}$ were analyzed by the AM1 method as included in the GAUSSIAN 98 package [17]. It is known that the semiempirical method AM1 produces realistic structures of stable conformations especially of hydrocarbons and gives the correct order of their stability [18]. However, this is less certain for organometallic compounds. Yet, the results of the AM1 calculations of the transition metal complexes can be still helpful in a discussion of experimental results. The "model"-cyclophanes **1***–**4***, lacking the methyl substituents at the etheno bridge, were used to make the calculation inexpensive. These methyl groups point away from the molecular cavity and are not expected to have a significant influence on the order stability of preferred conformations. The most stable conformations of **1***–**4*** are shown in Fig. 3, and some molecular parameters are given in Table 3. The [2.3]paracyclophan-11-en **1*** is a strained and almost rigid compound, as seen by the considerable twist of the two benzene rings between the para-C atoms shouldering the bridges. The two benzene units are only slightly spreading in **1***, and the distance $d(C_{b1}–C'_{b1})$ between the C atoms C_{b1} and C'_{b1} supporting the etheno bridge is 274.8 pm, whereas the distance $d(C_{b2}–C'_{b2})$ between the C atoms C_{b2} and C'_{b2} carrying the trimethylene bridge corresponds to 321.6 pm. With elongation of the oligomethylene bridge the cyclophanes become less strained, the spreading of



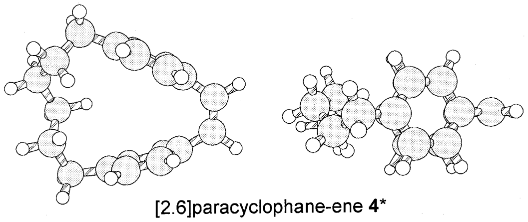
[2.3]paracyclophane-ene **1***



[2.4]paracyclophane-ene **2***



[2.5]paracyclophane-ene **3***



[2.6]paracyclophane-ene **4***

Fig. 3. Structure of $[2.n]$paracyclophane-enes calculated by AM1.

the two benzene units increases, and the molecules become more flexible. Thus, **2*** displays distances $d(C_{b1}–C'_{b1})$ and $d(C_{b2}–C'_{b2})$ of 278.9 and 391.4 pm, respectively, and in particular the distance $d(C_{b2}–C'_{b2})$ between the C atoms anchoring the oligomethylene bridge is increased by elongation of the oligomethylene bridge. Further elongation of this bridge increases $d(C_{b1}–C'_{b1})$ and $d(C_{b2}–C'_{b2})$ eventually to 280.2 and 415.1 pm, respectively, in **4***. Further, in contrast to the short oligomethylene bridges of **1*** and **2***, the pentamethylene bridge of **3*** and the hexamethylene bridge of **4*** are flexible and allow an increase of the spreading between the two benzene rings. Thus, the host cyclophanes **3*** and **4*** have the possibility to enlarge their molecular cavity further if this is required by a guest.

A priori the addition of transition metal ions to the cyclophanes **1–4** can yield several stable structures. The most simple one would be an ion/molecule complex (**IMC**) in which the metal cation is attached to the organic molecule simply by electrostatic ion/dipole and ion/induced dipole forces, and in which the components are more or less unrestricted in their mutual orientation. In contrast, an adduct ion in which the metal ion is embodied in the cavity of the cyclophane would be an essentially rigid structure. This "in" complex (**IC**) is related to the sandwich complexes observed for many transition metal ions and benzene or other arenes [5,6,10], although the two benzene rings of the $[2.n]$paracyclophanes are not parallel and are restricted in their orientation toward the central metal ion. A third possible structure displays the transition metal ion as sitting outside of the cyclophane on top of one benzene ring. Therefore, in this "out" complex (**OC**) the metal ion is coordinated only to one benzene ring. Finally, in a forth structure the coordination site of the transition metal ion can be the double bond of the etheno bridge outside of the cyclophane cavity, and in this "side on" complex (**SC**) the binding of the metal may be further assisted by the benzene rings. The electronic energy of the complexes of the transition metal ions Fe^+, Co^+, and Ni^+ by AM1 are given in Table 4, and typical structures of the adduct ions are presented in Figs. 4 and 5.

Besides structures of type **IMC**, in which the distance of metal ion to the cyclophane is always $>$400 pm and whose geometry are apparently not very well defined and varies in reiterated calculations, structures of the type **IC**, **OC**, and **SC** are found as potential energy minima for all model systems consisting of the transition metal ion M^+ (M = Fe, Co, Ni) and the cyclophanes **1***, **2***, **3***, and **4***. In the structures of the out complexes **OC** the metal ion is located on top of one benzene ring at a distance $d(M^+ - R)$ of 215 ± 5 pm of the metal ion to the center of this ring, somewhat larger than the coordination radii given in the literature for Fe^+, Co^+, and Ni^+ [11]. In all systems the structures of type **OC** are not the energetically most favored one. The most, stable structures are either in complexes of type **IC** or side-on complexes of type **SC**. Some parameters of the calculated geometry of the in complexes **IC** are

Table 4
AM1-SCF energies (E_l in Hartrees) of complexes of transition metal and [2.*n*]parapcyclophane-enes **1***–**4***

		Transition metal ion		
[2.*n*]paracyclophane-ene	Structure	Fe^+	Co^+	Ni+
1* ($n = 3$)	IC	0.102 796	0.101 848	0.091 517
	OC	0.108 873	0.108 542	0.106 561
	SC1	0.106 787	0.107 086	0.090 441
2* ($n = 4$)	IC	0.079 867	0.079 006	0.074 953
	OC	0.084 322	0.083 598	0.083 159
	SC1	0.082 762	0.082 370	0.077 482
	SC2	0.078 422	0.077 455	0.068 763
3* ($n = 5$)	IC	0.064 265	0.061 764	0.060 071
	OC	0.072 469	0.072 213	0.069 680
	SC1	0.070 990	0.070 445	0.068 880
	SC2	0.066 496	0.065 764	0.062 936
4* ($n = 6$)	IC	0.039 283	0.037 090	0.033 938
	OC	0.051 370	0.050 760	0.049 343
	SC1	0.049 485	0.048 705	0.046 889
	SC2	0.043 612	0.041 865	0.039 222

presented in Table 5. For complexes of type **IC** of the cyclophane **1*** the metal ion is almost extruded from the molecular cavity, and the two benzene rings are more or less rotated so that the molecular cavity forms a bowl for the coordination of the metal ion, in particular in the complex of Ni^+. Obviously, the molecular cavity of **1*** is not large enough to incorporated Fe^+, Co^+, or Ni^+. For the larger cyclophanes **2***–**4*** AM1 finds structures of the type **IC** with the metal ion incorporated into the molecular cavity between the dispersed benzene rings. In the case of **2*** the tetramethylene bridge is stretched considerably, so that $d(C_{b2}–C_{b2'})$ increases by 46 pm compared to the free ligand **2***. Further, the benzene rings are somewhat tilted so that the size of the molecular cavity is increased and slightly bowl shaped. Clearly, the incorporation of the metal ion causes strain to the cyclophane molecule. To minimize the strain, the metal ion is dislocated from the center of the benzene rings to the rim of the rings following the bearing of the benzene rings. As a consequence of this conformational strain the most stable structure of the complexes of cyclophane **2*** are of type **SC**, in which the metal ion has been almost completely propelled out of the cyclophane cavity in the direction of the tetra-

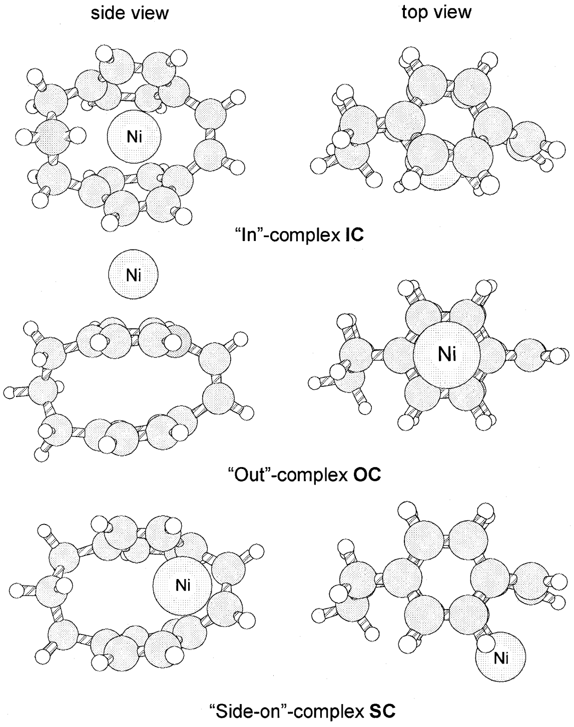


Fig. 4. Structures of complexes [Ni · **1***]$^+$ calculated by AM1.

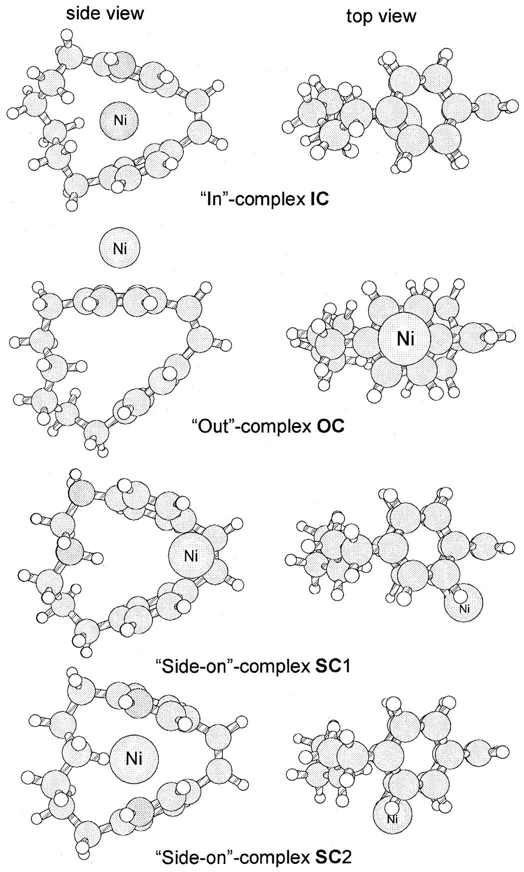


Fig. 5. Structures of complexes [Ni · **4***]$^+$ calculated by AM1.

methylene bridge (structure **SC2**), whereas a structure **SC1** with the metal ion located outside of the cyclophane cavity near to the etheno bridge is less stable. Analogous conformations are calculated for the complexes of cyclophanes **3*** and **4***. The in complex **IC** is calculated to be the most stable species for most (**M** · **3***)$^+$ and (**M** · **4***)$^+$, in line with the resemblance of structure **IC** with the stable sandwich complexes of benzene and PAH with transition metal ions. The distances $d(\mathrm{C}_{b1}$–$\mathrm{C}_{b1'})$ and $d(\mathrm{C}_{b2}$–$\mathrm{C}_{b2'})$ in these **IC** complexes are not significantly different from the free cyclophanes **3*** and **4*** (compare data from Tables 4 and 5). However, the metal ions are always displaced toward the rim of the benzene rings. Further, stable structures of type **SC** were obtained as potential energy minima for (**M** · **3***)$^+$ and (**M** · **4***)$^+$. These structures **SC** do not show the expected close contacts of the metal ion to the etheno bridge. Instead, the metal ion is located aside the molecular cavity with short contacts to a (formal) double bond of each of the benzene rings. Structures of this type are unknown for complexes of transition metals with benzene or PAH, and sandwich complexes are preferred even in the case of the corresponding complexes of 1.n-diphenylalkanes [19]. However, the two benzene rings of a paracyclophane are already kept in a sandwich structure by the two bridges, so that a side-on complex **SC** enables an interaction of the metal ion with both benzene groups, but avoids the additional strain associated with the incorporation of the metal ion into the molecular cavity.

Experimental evidence for the structures of the complexes [M(cyclophane)]$^+$ is available from CID experiments. Fig. 6 shows as typical examples the series of spectra obtained from the adduct ions of Co$^+$ with cyclophanes **1**–**4**. With exception of the complexes of Ag$^+$, which eliminate abundantly AgH during CID, none of the complexes dissociates predominantly into the components M$^+$ and cyclophane, M and cyclophane$^{\cdot+}$, or MH$_n$ and (cyclophane–nH)$^{\cdot+}$

Table 5
Molecular geometry parameters[a] of structures of in complexes **IC** of Fe$^+$, Co$^+$, and Ni$^+$ with cyclophanes **1***–**4*** calculated by AMI

	Fe$^+$			Co$^+$			Ni$^+$		
Cyclophane	d (C$_{b1}$–C$_{b1}$) (pm)	d (C$_{b2}$–C$_{b2}$) (pm)	∢Θ (deg)	d (C$_{b1}$–$_{b1}$) (pm)	d (C$_{b2}$–C$_{b2}$) (pm)	∢Θ (deg)	d (C$_{b1}$–C$_{b1}$) (pm)	d (C$_{b2}$–C$_{b2}$–C$_{b2}$) (pm)	∢Θ (deg)
1*	275.8	324.7	103	275.1	324.6	103	300.2	356.4	105.5
2*	293.3	436.0	111	293.4	437.1	111	294.1	438.9	112
3*	290.3	450.7	112	290.4	452.0	111.5	290.9	453.5	112
4*	285.5	486.5	114.5	285.2	487.0	114.5	285.1	487.4	114.5

[a] For definition see structure formula of Table 3.

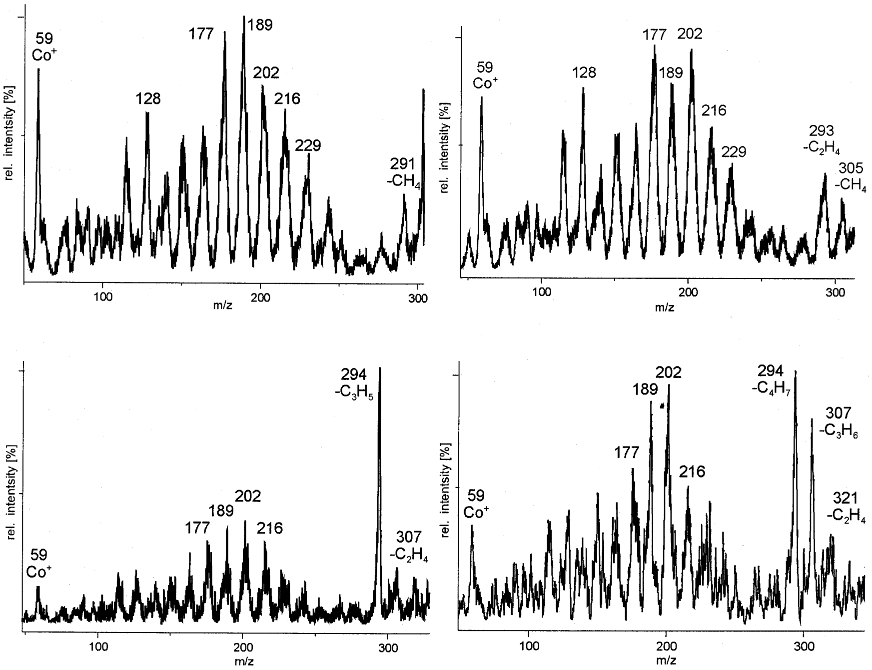


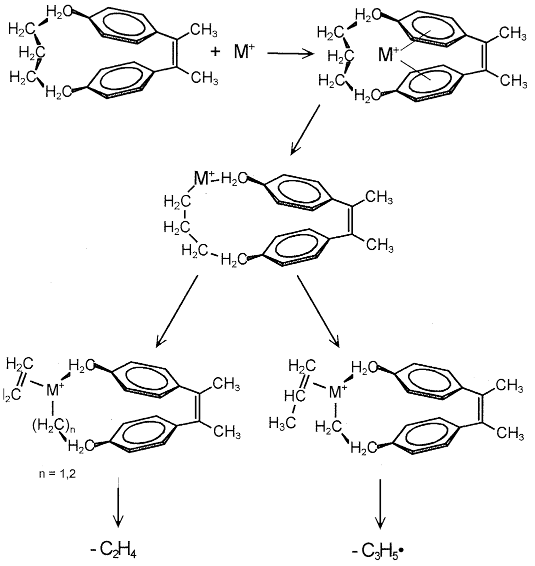
Fig. 6. CID mass spectra of adducts of (a) [Co · **1**]$^+$, (b) [Co · **2**]$^+$, (c) [Co · **3**]$^+$, and (d) [Co · **4**]$^+$.

during CID. Instead, the spectra display mostly abundant and not very well resolved signals owing to fragment ions of the cyclophane. This excludes structures of type **IMC** which are expected to dissociate readily into the components. Rather, the transition metal ion is strongly bound to the cyclophane in the complexes as in structures **OC**, **IC**, and **SC**. The coordination of M^+ to only one of the benzene rings of the cyclophane in structures of type **OC** should give these out complexes properties comparable to monomeric complexes of M^+ with benzene or planar PAH. The characteristic property of these complexes is the formation of dimeric complexes $[M(arene)_2]^+$. This behavior is observed only for the complexes of (**Ag** · **1***)$^+$ and (**Co** · **1***)$^+$. Because the molecular cavity of **1** is too small to accept Ag^+ and probably even Fe^+ and Co^+ with formation of an in complex **IC**, the out complex **OC** may be a choice for these systems. However, a preferred dissociation into the components during CID has been reported also for monomeric complexes [M(benzene)]$^+$ [5]. Here, this is not observed for the complexes of $M^+ = Fe^+$, Co^+, Ni^+, and Cu^+ with cyclophanes **1**. This result points to structures corresponding to in complexes **IC** or side-on complexes **SC** also for these species, in spite of the strain in (**M** · **1***)$^+$. In fact, the excessive fragmentation of the complexes (**M** · **1***)$^+$ and (**M** · **2***)$^+$ during CID agrees with the decomposition of strained species. It is known from transition metal complexes of 1,*n*-diphenylalkanes that such complexes rearrange on collisional activation and that the sandwiched metal ion inserts in C–H bonds and likely also in benzylic C–C bonds [19,20]. The metastable ions of the Fe^+ sandwich complex of 1.4-diphenylbutane eliminate H_2, C_2H_4, and C_7H_8. The in complexes **IC** with asymmetrically positioned metal ions and especially the side-on complexes **SC** with the metal ion located outside the molecular cavity near the polymethylene bridge of the cyclophanes are disposed for analogous rearrangements. However, the CID mass spectra of complexes of cyclophane **2**, which contains a $(CH_2)_4$ bridge between the two benzene rings as 1,4-diphenylbutene, display only small signals for the losses of CH_4 and C_2H_4 [*m/z* 305 and *m/z* 293 in Fig. 6(b)], but groups of intense signals of fragment ions of the cyclophane around *m/z* 216($C_{17}H_{12}^{\cdot+}$), *m/z* 202($C_{16}H_{10}^{\cdot+}$), *m/z* 189($C_{15}H_{9}^{+}$), and *m/z* 177($C_{14}H_{9}^{+}$). A similar severe degradation by CID is observed for the complexes of **1** containing the shorter $(CH_2)_3$ bridge and yielding again the series of abundant ions *m/z* 216–*m/z* 177 [Fig. 6(a)]. Clearly, fragment ions of this type must have lost parts of the oligomethylene bridge as C,H fragments and probably also methyl substituents besides the neutral metal [14]. Supposedly the strained complexes $(\mathbf{M \cdot 1^*})^+$ and $(\mathbf{M \cdot 2^*})^+$ decompose readily by CID to these fragment ions consisting of the dimethylstilbene moiety as the "hard core" of the cyclophane because of the release of steric strain during the rearrangements. In the case of the complexes $(\mathbf{M \cdot 3^*})^+$ and $(\mathbf{M \cdot 4^*})^+$ of the less strained cyclophanes **3** and **4** the spectra generated by CID exhibit a base peak owing to fragment ions containing still the metal ion. In the case of the Co^+ adduct of **3** this is the ion $[Co(C_{18}H_{19})]^+$, *m/z* 294, generated by loss of C_3H_5, and of the Co^+ adduct of **4** the ions $[Co(C_{18}H_{19})]^+$, *m/z* 294, and $[Co(C_{19}H_{20})]^+$, *m/z* 307, formed by losses of C_4H_7 and C_3H_6, respectively [see Fig. 6(c) and (d)].

The formation of these fragment ions can be explained by the mechanisms similar to those proposed by Raabe et al. for the fragmentation of the complexes of 1.*n*-diphenylalkanes with transition metals [19]. The essential step is the insertion of the metal ion into benzylic bonds of the ligand followed by *β*-hydrogen transfer and rearrangements. The special feature of a cyclophane ligand is the presence of a second bridge between the benzene rings. This prevents loss of C_7H_8 as in the case of the 1.*n*-diphenylalkane ligands and restricts fragmentation to the loss of (C,H) fragments from the oligamethylene bridge (Scheme 3).

4. Conclusion

The uncomplicated formation of complexes of transition metal ions $M^+ = Cu^+$ and Ag^+ with cyclophanes was expected from the well know ability of these ions to generate adducts with aromatic hydrocarbons [4,20]. A first special feature of this study is the observation that SIMS of dry mixtures of salts of a transition metal and a cyclophane can be conveniently used to produce these complex ions in the gas phase not only from salts of Ag and Cu but also from other first row transition metals with exception of Zn. A second one is that only the monomeric complexes [M(cyclophane)]$^+$ are formed with the exception of Co^+ and Ag^+, which produce also dimeric complexes [M(cyclophane)$_2$]$^+$ which are typical for the reactions of planar PAH with transition metal ions [5,10,11,19]. The generation of adduct ions in the mass spectra obtained under the conditions of SIMS used here are explained readily by ion/molecule reactions in the gas phase of the SIMS ion source between the sputtered transition metal ions and neutral molecules of the cyclophanes **1**–**4** evaporating from the target holder which is heated by the impact of Cs^+ ions of the primary ion beam. A competing ion/molecule reaction is charge transfer to generate molecular ions of the cyclophanes. The peaks of [M(cyclophane)]$^+$ and (cyclophane)$^{\cdot+}$ are indeed the only abundant signals in the high mass region of the SIMS spectra obtained from mixtures of the salts of transition metals and **1**–**4**. Further, these competing ion/molecule reactions



Scheme 3.

explain the failure of Zn^+ to form complexes with **1**–**4** since charge transfer prevails because of the high IE(Zn).

If the adducts $[M(cyclophane)]^+$ are activated by collision with He, the resulting mass spectra show peaks of fragment ions arising from the loss of small hydrocarbon fragments and from the loss of the metal atom and excessive fragmentation of the cyclophane moiety, but no substantial dissociation into the original components is observed. This is a clear indication that the metal ions are strongly bonded in these adducts as expected for an in complex structure **IC** with the metal ion buried in the cavity of the cyclophane. This structure is further evidenced by a different behavior on CID of the complexes of cyclophanes **1** and **2** on the one side and complexes of cyclophanes **3** and **4** on the other side. Complexes of **1** and **2**, which expose a small molecular cavity and can form only strained in complexes, undergo predominantly extensive fragmentation to hydrocarbon ions on CID, whereas complexes of **3** and **4** with a larger molecular cavity and less strain fragment on CID abundantly by loss of small hydrocarbons from the oligomethylene bridge and retain the metal ion. Calculations of the structure and conformation of the complexes of Fe^+, Co^+, and Ni^+ using the semiempirical AM1 method show that the structure of the complexes may be either an asymmetric in complex with the metal ion shifted toward the border of the cavity close to the oligomethylene bridge or a side-on complex **SC** with the metal ion located outside of the cavity but still interacting with both benzene rings. Such structures allow still an insertion of the metal ion into benzylic bonds on collisional activation, which very likely precede CID, because of the close contacts of the metal ion to atoms of the oligomethylene bridge (see Figs. 4 and 5). Formation of in or side-on complexes, in which the metal ion is more or less concealed by the cyclophane ligand, gives also a convincing explanation for the observation of only monomeric adducts $[M(cyclophane)]^+$. This is in line with the observation of a “cavity effect” in the complexation of the macrocyclic tricyclyne with metal ions by Pozniak and Dunbar [10], and clearly the attachment of a second cyclophane ligand to $[M(cyclophane)]^+$ is sterically hindered in structures of type **IC** and **SC**.

The extent of competition between complex formation and charge transfer as well as experiments analyzing a direct competition between two transition metal ions for complexation of the same cyclophane show that complex formation increases distinctly in the series $Fe^+ \ll Co^+ < Ni^+ \ll Cu^+ \ll Ag^+$, in agreement with the large affinity of Cu^+ and Ag^+ to aromatic compounds known from the literature. With respect to the dependence of complex formation on the size of the molecular cavity of the cyclophanes, cyclophane **1**, containing only a trimethylene bridge and exhibiting therefore only a small cavity, receives least all metal ions studied, whereas **3** and **4** are a good host for the metal ions. The selectivity between **1** and **3** or **4** is not striking, however, and less than a factor of 10. Further, there is no clear dependence on the cyclophane selectivity on the nature of the metal ion. These small effects may be partly due to the fact that the covalent radii of the metal ions studies are not very different, with the exception of Ag^+, but certainly also due to the different structures accessible to the adducts of the metal ions and cyclophanes **1**–**4**. According to the AM1 calculations, complex formation does not depend on a “perfect fit” of the molecular cavity of the host cyclophane and of the size of the guest metal ion. Thus, no sharp “yes/no” boundary for the ability to form a complex can be expected for this type of ligand.

Acknowledgements

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