

Competitive Complexation of Gaseous Mn^{II} by 1,10-Phenanthroline, 2,2'-Bipyridine, and 4,5-Diazafluorene

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Complexes of Mn^{II} with 1,10-phenanthroline (phen) and 2,2'-bipyridine (bipy) are investigated by means of electrospray ionization (ESI) mass spectrometry. Under the conditions used, [MnL_n]²⁺ with *n* = 2 and 3, [MnL_nCl]⁺ with *n* = 0–2, and [Mn₂L_nCl₃]⁺ with *n* = 2 and 3 are produced (where L = phen or bipy). The collision-induced dissociation (CID) spectra of the mass-selected ions show various dissociation pathways, most notable among them is the reduction of the ligated Mn^{II} to Mn^I by intracomplex electron transfer. CID experiments of mixed-ligand complexes formed upon ESI from solutions which contain both phen and bipy exhibit preferential eliminations of bipy, indicating that bipy is a significantly weaker ligand for Mn^{II} than phen. This effect is mainly attributed to the flexibility of the bipy ligand concomitant with thermodynamic control in ion dissociation. To support this hypothesis, mixed complexes with some methylated derivatives as well as those containing 4,5-diazafluorene (daf) are examined also. Interestingly, the differences between the ligands diminish in charge-separation reactions of dicationic Mn^{II} complexes, due to the joined operation of thermodynamic as well as kinetic effects. In addition, the complexes [Mn(bipy)]⁺, [Mn(phen)]⁺, [Mn(bipy)]²⁺, [Mn(phen)]²⁺, and [Mn(bipy)(phen)]²⁺ are computed using the *m*PW1PW91 hybrid density functional along with the Stuttgart–Cologne-type pseudopotential and basis-set suite, and relative energies for charge-separation reactions and losses of neutral ligands are evaluated.

1. Introduction

The cationization of neutral solvent molecules by association with metal cations has received great attention over the past few years both from the experimental and from the theoretical points of view.^{1,2} Electrospray ionization (ESI) developed by Yamashita and Fenn^{3,4} has provided an easy access to multiply charged ions in the gas phase and thus has been extremely helpful in the characterization of multiply charged ions generated from large, native solvation shells present in solution.

The nitrogen heterocycles 1,10-phenanthroline (phen) and 2,2'-bipyridine (bipy) are among the most widely utilized chelate ligands in coordination chemistry both in the liquid phase^{5–11} as well as in the gas phase.^{12–21} These ligands

provide two sp²-hybridized nitrogen atoms whose in-plane, unshared electron pairs may act cooperatively in binding

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cations.^{22,23} Although phen and bipy have very similar structures, there is a difference between their chelating ability, which is mostly attributed to the different geometry of the free molecules.^{24–26} With the discovery that transition-metal complexes of phen and bipy are capable of site-specific DNA interactions through external binding, groove binding, or intercalation, new fields of applications have emerged which include biology and medicine.^{27–30}

The divalent manganese cation forms complexes with several ligands in aqueous solutions, but the equilibrium constants are low compared to those of other dications (e.g., Fe^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+}) because of the larger radius of Mn^{2+} (75 pm). The ionization energy of Mn^+ amounts to 15.64 eV;³¹ hence, not surprisingly, partially or nonsolvated dication complexes of manganese can undergo charge reduction via intracomplex electron transfer from the ligand to Mn^{2+} , with the dication complexes becoming less stable with decreasing size.³² Complexes of Mn^{2+} with organic molecules in the gas phase have been investigated by many researchers in the last years using ESI mass spectrometry.^{33–41} Little information exists, however, on the complexation of Mn^{2+} by phen and bipy in the gas phase. Vachet and Callahan⁴² focused on monocationic complexes of the type $[\text{MnL}_n\text{Cl}]^+$ with $\text{L} = \text{phen}$ and bipy .⁴³ Here, we report on the complexation ability of phen and bipy toward Mn^{II} using

ESI mass spectrometry with particular attention to the similarities and differences of these two prototypical nitrogen chelate ligands. The experimental findings are complemented by density functional theory calculations.

2. Experimental and Computational Details

Apparatus and Procedures. The experiments were performed with a VG BIO-Q instrument which consists of an ESI source followed by a mass spectrometer of QHQ configuration (Q quadrupole, H hexapole) as described elsewhere.^{44,45} For each ion of interest, the instrument parameters were optimized for maximum ion abundances. Typical adjustments were capillary voltage 3.6 kV, HV lens (counter electrode) 30 V, cone voltage 0–70 V, RF lens 0.1 V, skimmer 1.0 V, and skimmer-lens offset 5 V. In the experiments, millimolar solutions of MnCl_2 were introduced via a syringe pump (flow rate of 5 $\mu\text{L}/\text{min}$) to the fused-silica capillary of the ESI source. Nitrogen was used as nebulizing and drying gas at a source temperature of 90 °C. The mass range (m/z) examined in this study was usually 30–1000.

Collision-induced dissociation (CID) experiments were performed with xenon at various collision energies ($E_{\text{lab}} = 0–70$ eV) at a collision gas pressure of ca. 3×10^{-4} mbar. The laboratory collision energies were converted to the center-of-mass frame, $E_{\text{CM}} = z[m/(M + m)]E_{\text{lab}}$, where z is the ion's charge and m and M are the masses of the collision gas and the ionic species, respectively. For CID, the ions of interest were mass selected using Q1, interacting with xenon in the hexapole collision cell, while scanning Q2 to monitor the ionic fragments. As pointed out previously,⁴⁴ the VG Bio-Q does not allow quantitative threshold information to be extracted directly from CID experiments because of several limitations of the commercial instrument. Even at $E_{\text{lab}} = 0$ eV, for example, nonnegligible ion decay is observed for weakly bound ions which is in part attributed to the presence of collision gas not only in the hexapole but also in the focusing regions between the mass analyzers. To a first approximation, however, the energy dependence of the CID spectra can be reproduced quite well by a sigmoid function⁴⁶ which allows extraction of some semiquantitative information about the energetics of the ions examined. In the present paper, a more phenomenological approach is used which is sufficient to order the coordination abilities of phen and bipy to Mn^{2+} .

Ligated Mn^{2+} ions were generated from solutions of MnCl_2 (1×10^{-4} mol·dm⁻³) in 1:1 mixtures of water/methanol containing (a) 1,10-phenanthroline (5×10^{-4} mol·dm⁻³), (b) 2,2'-bipyridine (5×10^{-4} mol·dm⁻³), and (c) an equal concentration of 1,10-phenanthroline and 2,2'-bipyridine (5×10^{-4} mol·dm⁻³). All of the solutions were prepared by weight with an accuracy of ± 0.0001 g. Similar conditions were applied to produce Mn^{II} complexes with 4,5-diazafluorene (daf).

Materials. Methanol (Fluka, >99.9%) was spectral grade. The water was doubly distilled, and the specific conductivity was lower than 0.40 $\mu\text{S}\cdot\text{cm}^{-1}$ at 20 °C. Compounds 1,10-phenanthroline (Acros Organics, >99.0%), 2,2'-bipyridine (Sigma, >99.0%), and manganese chloride tetrahydrate (Aldrich, >99.99%) were used without further purification.

Compound 4,5-diazafluorene was prepared from 1,10-phenanthroline in two steps. At first, 4,5-diazafluorene-9-one was synthe-

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sized according to a method described by Plater et al.⁴⁷ To this end 1,10-phenanthroline (2 g, 0.011 mol) and KOH (2 g, 0.036 mol) were dissolved in distilled water (150 mL) and brought to reflux. A hot aqueous solution of KMnO₄ (5 g, 0.032 mol, 80 mL) was added dropwise over 2 h with stirring. After removal of MnO₂, the filtrate was cooled, extracted with chloroform, and dried over anhydrous MgSO₄, and the solvent was removed at reduced pressure. Recrystallization from acetone yielded 0.5 g (25%) of yellow crystals of 4,5-diazafluoren-9-one: mp 212–213 °C. ¹H NMR spectrum (400 MHz, CDCl₃): δ_H 8.81 (d, 2H), 7.99 (d, 2H), and 7.35 (dd, 2H) was in good agreement with the literature values.⁴⁸ The subsequent reduction to 4,5-diazafluorene was performed following a method described by Thummel et al.⁴⁹ To this end, a mixture of 4,5-diazafluoren-9-one (0.15 g, 0.0008 mol) and hydrazine hydrate (0.07 g, 0.0014 mol) was heated at 210 °C for 6 h; after cooling, the mixture was extracted with CH₂Cl₂, dried over anhydrous MgSO₄, and concentrated. Chromatography on silica gel with ethyl acetate as the eluent yielded 0.030 g (23%) of 4,5-diazafluorene, whose structure was confirmed by ¹H NMR spectrometry (400 MHz, CDCl₃): δ_H 3.86 (s, 2H), 7.29 (dd, 2H), 7.87 (d, 2H), and 8.73 (d, 2H).⁴⁷

Computations. The density functional theory (DFT) calculations were carried out utilizing the Gaussian 03 program package,⁵⁰ and the *m*PWP1PW91 hybrid density functional⁵¹ was employed throughout. Studies of Porembski and Weisshaar^{52,53} suggest that this method is more suitable to describe coordinatively unsaturated transition-metal compounds than the commonly employed B3LYP approach.⁵⁴ This is especially true for transition-metal arene complexes,⁵⁵ where charge-induced ion–dipole and ion–quadrupole interactions play a crucial role.⁵⁶ The atoms were described by the single-particle basis sets of Dolg and colleagues.^{57,58} The basis sets of carbon and nitrogen were augmented by one d-polarization

function with exponents of 0.75 and 0.80, respectively.⁵⁹ For hydrogen, Dunning's polarized double- ζ basis set was used.⁵⁹ The inner core electrons of the non-hydrogen atoms (1s for C and N and 1s2s2p for Mn) were replaced by the corresponding relativistic pseudopotentials. All of the local minima were verified through analysis of the Hessian matrix. Energies are corrected for zero-point vibrational energy contributions.

3. Results and Discussion

The focus of this paper is on mixed complexes of Mn^{II} with bipy and phen ligands. At the outset, however, a brief description of the types of complexes formed with either one of these ligands and their general fragmentation patterns is given.

3.1 Complexes of Mn²⁺ with either phen or bipy. Solvated gaseous cations formed upon ESI-MS of water/methanol mixtures which contain MnCl₂ and a 5-fold excess of 1,10-phenanthroline or 2,2'-bipyridine were in both cases of the same general type. Prevalent complexes correspond to the dications [MnL_{*n*}]²⁺ with *n* = 2 and 3, the monocations [MnL_{*n*}Cl]⁺ with *n* = 0–2, and the chloro-bridged clusters [Mn₂L_{*n*}Cl₃]⁺ with *n* = 2 and 3 (where L = phen or bipy). In addition, complexes of the general formula [MnL(CH₃-OH)_{*n*}Cl]⁺ (with *n* = 1 and 2) were observed, which are not pursued any further. Notably, the type of the ions formed upon ESI differs from what would have been expected based on the solution chemistry of these manganese species. In solution, phen and bipy are stronger ligands than Cl[−], and a predominance of the dications [MnL_{*n*}]²⁺ has been demonstrated.⁶⁰ In the gas phase, however, solvent molecules do not exist to stabilize the Cl[−] ions; thus, the Coulombic interactions between the counterions and Mn²⁺ are stronger than the dative electron-sharing interactions between the metal cation and the neutral molecules phen or bipy.⁴² As a consequence, both the dications [MnL_{*n*}]²⁺ as well as the monocations [MnL_{*n*}Cl]⁺ are observed in the gas phase. In addition, the ESI spectra of the MnCl₂ solutions in the negative ion mode reveal that ions of the general type [Mn_{*n*}Cl_{2*n*+1}][−] (with *n* = 1–3) prevail among the anionic species.

The overall appearance of electrospray mass spectra is heavily affected by the conditions of ionization. One of the most decisive parameters is the cone voltage (*U*_c) which determines the amount of collisional activation of the ions formed initially from the electrospray during the transfer to the high-vacuum system. At low voltages, ionization is gentle, and the observed gaseous ions include species that exist in the liquid phase. At higher cone voltages, the observed ions result from multicollisional fragmentation reactions. Specifically, the ESI spectra display the formation of gaseous ions [MnL₃]²⁺, [MnL₂Cl]⁺, and [Mn₂L₃Cl₃]⁺ in a cone voltage region of *U*_c = 0–20 V, while [MnL₂]²⁺, [MnLCl]⁺, and [Mn₂L₂Cl₃]⁺ prevail at *U*_c = 30–40 V. Above *U*_c = 50 V, the diatomic cation MnCl⁺ and the reduced complex [MnL]⁺ appear as new products, and finally

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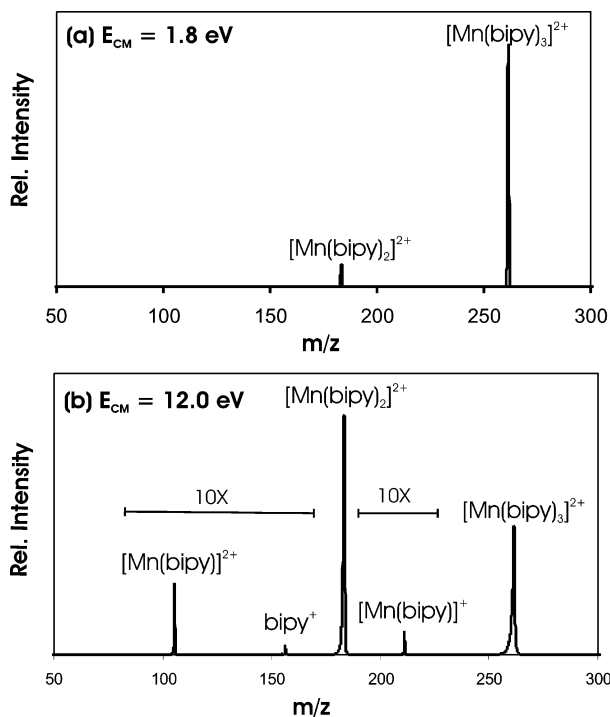
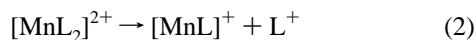
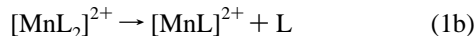
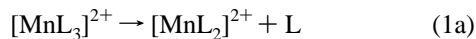


Figure 1. CID spectra of mass-selected $[\text{Mn}(\text{bipy})_3]^{2+}$ at variable collision energies (E_{CM} in eV). Note that the stoichiometry of reaction 2 suggests the formation of equal amounts of $[\text{Mn}(\text{bipy})]^{+}$ and bipy^{+} , whereas much more $[\text{Mn}(\text{bipy})]^{+}$ is observed experimentally because of increased scattering of the lighter bipy^{+} fragment as a result of the energy released in the Coulombic explosion.

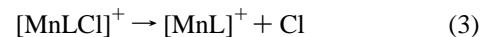
bare Mn^{+} prevails at high cone voltages ($U_c > 70$ V). Failure to observe a peak corresponding to the monoligated dication $[\text{MnL}]^{2+}$ in the ESI mass spectra is not too surprising. Most probably, the $[\text{MnL}]^{2+}$ dications are effectively depleted by electron transfer from the ligand to manganese followed by charge-separation reactions occurring in the cone region where additional solvent molecules are still present.⁴⁵

Gas-phase decomplexation of the solvated Mn^{2+} cations is probed by means of collision-induced dissociation using xenon as a collision gas. The CID spectrum of mass-selected $[\text{MnL}_3]^{2+}$ shows successive eliminations of ligands according to reactions 1a and 1b until the formation of the monoligated dication $[\text{MnL}]^{2+}$.

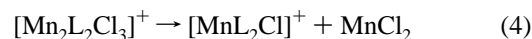


As an example for the fragmentation behavior of the multiply solvated dications, two CID spectra of $[\text{Mn}(\text{bipy})_3]^{2+}$ are shown in Figure 1. At low-collision energy ($E_{\text{CM}} \approx 1.8$ eV, Figure 1a), elimination of the first bipy ligand takes place. At elevated collision energy (Figure 1b), the CID spectrum reveals the elimination of a second bipy ligand and additional signals corresponding to bipy^{+} and $[\text{Mn}(\text{bipy})]^{+}$ and products of an electron-transfer/charge-separation process (reaction 2) which can be attributed to the fact that the ionization energy (IE) of Mn^{+} (15.64 eV)³¹ largely exceeds those of phen (8.30 eV)⁶¹ and (8.35 eV).⁶²

The dominant process observed upon CID of the monocations $[\text{MnL}_n\text{Cl}]^{+}$ ($n = 1, 2$) corresponds to the elimination of neutral ligands to finally yield diatomic MnCl^{+} . At the stage of $[\text{MnLCl}]^{+}$, homolysis of the Mn–Cl bond also occurs at elevated collision energies yielding the corresponding monoligated Mn^{I} complex (reaction 3).



Upon CID of the mass-selected binuclear complexes $[\text{Mn}_2\text{L}_3\text{Cl}_3]^{+}$, ligand loss is observed exclusively. At the stage of $[\text{Mn}_2\text{L}_2\text{Cl}_3]^{+}$, however, cluster degradation leads to neutral MnCl_2 concomitant with the formation of $[\text{MnL}_2\text{Cl}]^{+}$ (reaction 4).



The resulting mononuclear complex $[\text{MnL}_2\text{Cl}]^{+}$ then undergoes the fragmentation already described above. In analogy to a related study of binuclear Ni(II) complexes,⁶³ occurrence of reaction 4 suggests that the binuclear cluster is chloro-bridged with an nonsymmetrical distribution of the ligands, that is, $[\text{L}_2\text{Mn}(\mu\text{-Cl})_2\text{MnCl}]^{+}$. At first sight, it might appear surprising that these chlorine-rich binuclear complexes are formed in the presence of an excess of bipy and phen, respectively. A chemically intuitive rationale is provided by consideration of the charge balance of heterolysis in solution.⁶⁴ Thus, when MnCl_2 forms the dication $[\text{MnL}_n]^{2+}$, two chloride ions are liberated which can be bound by the metal halide present in solution to yield the $\text{Mn}_n\text{Cl}_{2n+1}^{-}$ species, which are indeed observed upon ESI in the negative-ion mode (see above). If $[\text{MnL}_n]^{2+}$ and MnCl_3^{-} happen to be present in the same droplet, ion–ion recombination is likely to occur upon shrinking of the droplet in the course of successive evaporation of the solvent. This scenario accounts quite well for the observation of this particular type of binuclear cluster as well as the proposed unsymmetrical pattern of phen/bipy and chlorine ligands.

3.2 Mixed-Ligand Complexes of Mn^{II} . For an investigation of the competition between phen and bipy in the ligation of Mn^{II} , solutions of MnCl_2 in water/methanol mixtures which contain equal amounts of both phen and bipy were subjected to ESI-MS. In addition to the complexes of Mn^{II} which only contain either phen or bipy, the source spectra at variable cone voltages revealed reasonably abundant signals of the corresponding mixed complexes.

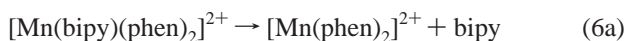
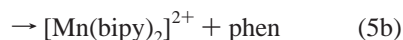
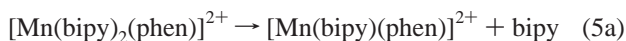
Upon CID of the mass-selected dications $[\text{Mn}(\text{bipy})_2(\text{phen})]^{2+}$ and $[\text{Mn}(\text{bipy})(\text{phen})_2]^{2+}$, respectively, the elimination of bipy (reactions 5a and 6a) predominates over that of phen (reactions 5b and 6b).

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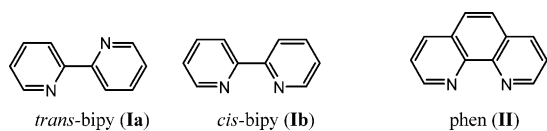
(62) Maier, J. P.; Turner, D. W. *Faraday Discuss. Chem. Soc.* **1972**, *54*, 149–167.

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Losses of phen are observed only at increased collision energies, but even then the elimination of bipy predominates. These results demonstrate that the binding of Mn²⁺ to phen is considerably stronger than to bipy.^{43a} This finding can be attributed to the different flexibilities of the free ligands. It is well-known that the two rings in bipy can rotate around the central C–C bond.^{65–69} When bipy approaches the metal cation to form a chelate complex, it undergoes transformation from the trans-conformation (structure **Ia**) to the less stable cis-conformation (structure **Ib**). In contrast, the backbone constrains phen to a cis-alignment of the nitrogen lone-electron pairs (structure **II**).²⁵



The cisoid form of bipy is 0.28 eV less stable than the trans conformer according to previous calculations.²⁵ Interestingly, the perfect coplanar arrangement of **Ib**, with a dihedral angle of 0°, even corresponds to a transition structure in the free ligand, which is 0.35 eV less favorable than structure **Ia**. Our mPW1PW91 calculations yield very similar energetics in that **Ib** with the rings tilted by about 30° is a minimum 0.30 eV above **Ia** and the coplanar structure represents a saddle point 0.33 eV less stable than **Ia**.

Upon decomplexation during CID, bipy can accordingly gain energy from a conformational change, whereas this is impossible for the rigid phen ligand. However, in the present mass spectrometric experiments the energy gain in the free ligands matters only if the conformational change occurs prior to the dissociation of the mixed complexes. Such a scenario is indeed quite likely to apply here because, prior to the loss of the bidentate nitrogen ligands, decomplexation of just one binding site can occur in the ions energized in the CID process. While still being bound to Mn²⁺ by the other N-atom, C–C bond rotation can occur, thus providing access to a thermodynamically more favorable dissociation channel.

As an example, the energy-dependent branching ratios upon CID of [Mn(bipy)(phen)₂]²⁺ and [Mn(bipy)₂(phen)]²⁺ are given in Figure 2. In the energy range studied, the elimination of neutral bipy is always favored for both

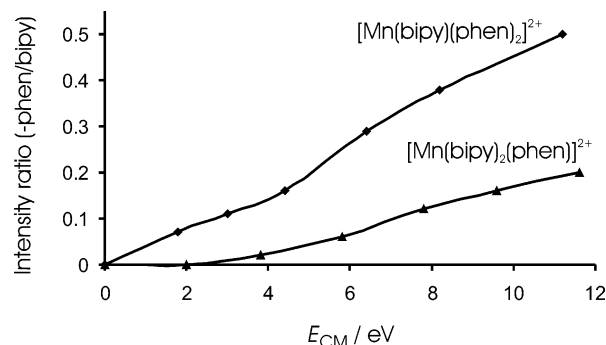


Figure 2. Ratio of the losses of phen and bipy upon CID of mass-selected dications [Mn(bipy)(phen)₂]²⁺ (◆) and [Mn(bipy)₂(phen)]²⁺ (▲) as a function of collision energy (E_{CM}).

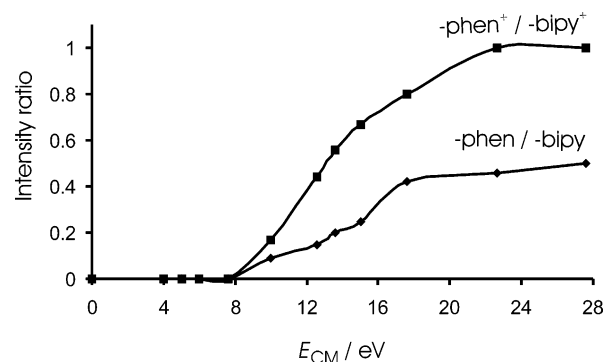
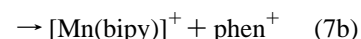


Figure 3. Ratios of the losses of phen⁺ and bipy⁺ as well as neutral phen and bipy, respectively, upon CID of mass-selected [Mn(bipy)(phen)]²⁺ as a function of collision energy (E_{CM}).

dications, although the preference slightly diminishes with increasing energy, as expected. CID of [Mn(bipy)(phen)₂]²⁺ reveals that even at increased collision energies ($E_{\text{CM}} \approx 10$ eV) and despite a statistical preference the loss of phen has only half of the abundance for the elimination of bipy. For the bipy-rich complex [Mn(bipy)₂(phen)]²⁺, the discrimination of the loss of the phen ligand is even more pronounced in that the abundance of [Mn(bipy)₂]²⁺ is only a fifth of that for [Mn(bipy)(phen)]²⁺ at $E_{\text{CM}} \approx 10$ eV.

Quite interesting is the CID behavior of the mixed dimer [Mn(bipy)(phen)]²⁺ (Figure 3). Also in this case, the loss of neutral bipy leading to [Mn(phen)]²⁺ is favored compared to the evaporation of phen throughout the collision-energy range studied, thus confirming once more the lower coordination ability of the bipy ligand. Parallel with the detachment of the neutral ligands, electron transfer from bipy or phen to Mn²⁺ can take place (reactions 7a and 7b) leading to the reduced complexes [Mn(phen)]⁺ and [Mn(bipy)]⁺ concomitant with the formation of the molecular cations bipy⁺ and phen⁺, respectively.



As shown in Figure 3, the branching ratios of the charge-separation reactions 7a and 7b vs that of the evaporation of neutral ligands differ quite significantly. Accordingly, the energetic difference between the phen and bipy channels is

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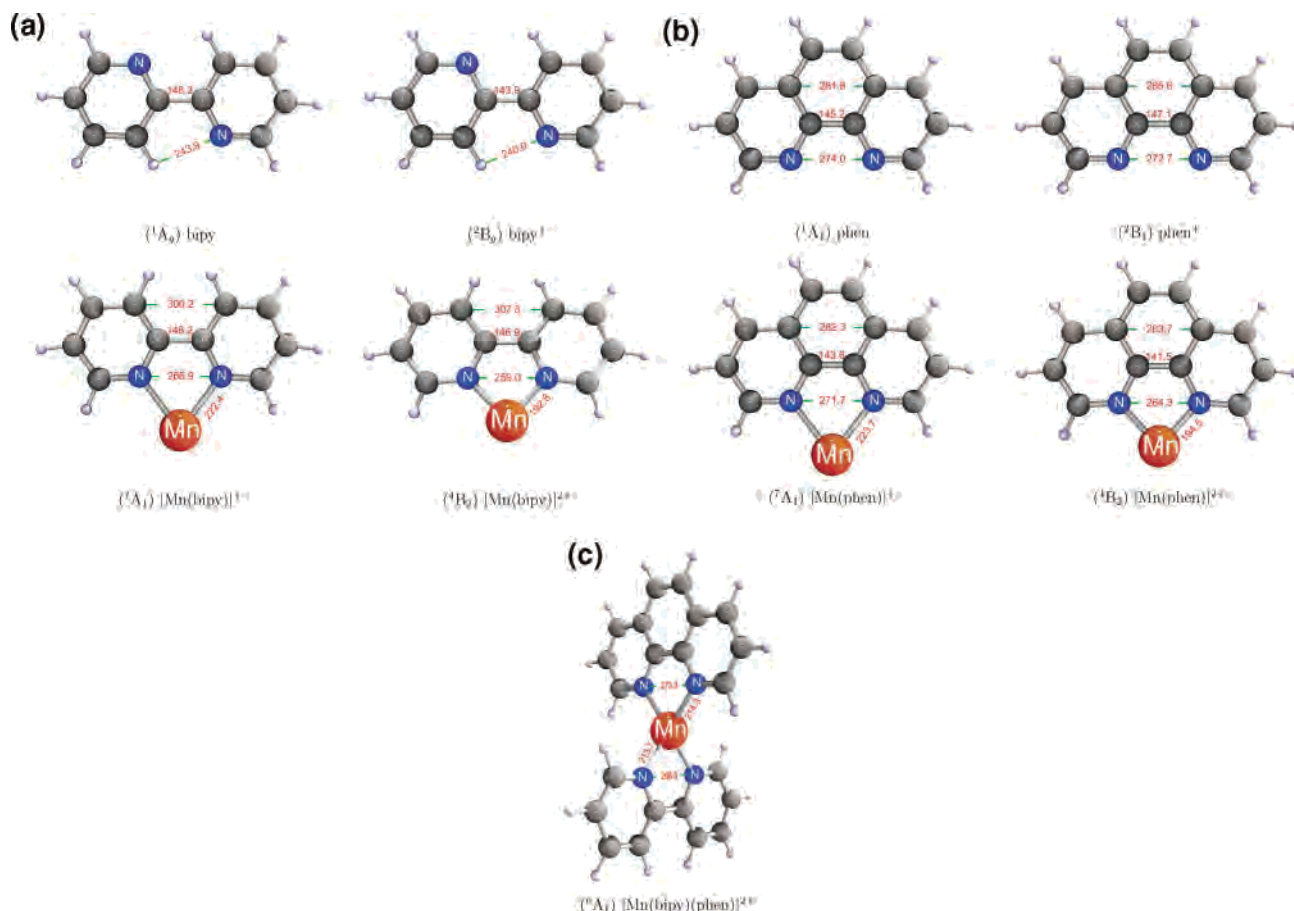


Figure 4. Computed geometries of (a) bipy, bipy⁺, [Mn(bipy)]⁺, [Mn(bipy)]²⁺, (b) phen, phen⁺, [Mn(phen)]⁺, [Mn(phen)]²⁺, and (c) [Mn(bipy)(phen)]²⁺. Selected distances are given in pm.

less pronounced in the losses of ionized ligands upon charge separation compared to the elimination of the neutral ligands. Hence, the mono- and dicationic complexes appear to show differential ligation.⁷⁰

To obtain further insight into the competing ligand losses from these dicationic manganese complexes with and without concomitant electron transfer, some relevant species were investigated theoretically using density functional theory. The monocations [Mn(bipy)]⁺ and [Mn(phen)]⁺ as well as the dications [Mn(bipy)]²⁺, [Mn(phen)]²⁺, and [Mn(bipy)(phen)]²⁺ have been computed, and the absolute energies as well as the ionization energies for the neutral and monocationic species are given in Table 1. All of the molecular species, with the exception of [Mn(bipy)(phen)]²⁺, were found to be planar, either of C_{2h} (neutral and cationic bipy) or of C_{2v} symmetry (Figure 4). The complexes have high-spin ground states; [Mn(bipy)]⁺ and [Mn(phen)]⁺ have septet multiplicity, and the corresponding dications [Mn(bipy)]²⁺ and [Mn(phen)]²⁺ are sextets. In either case, other multiplicities considered represent excited states being higher in energy by more than 0.9 eV (Table 1). In both the mono- and the dication complexes, the unpaired electrons reside almost exclusively on the metal center whereas the charge density is partially distributed across the arene ligand.

Table 1. Absolute Energies (E_{abs}) and Ionization Energies (IE) for [Mn(bipy)]⁺, [Mn(phen)]⁺, [Mn(bipy)]²⁺, [Mn(phen)]²⁺, [Mn(bipy)(phen)]²⁺, and Their Fragments^a

| species | state | $E_{\text{abs}}/\text{hartree}$ | IE/eV | |
|--------------------------------|-----------------------------|---------------------------------|-----------|--------------------|
| | | | this work | exp |
| Mn | ⁶ S | -104.346992 | 7.15 | 7.43 ^b |
| Mn ⁺ | ⁷ S | -104.084245 | 15.99 | 15.64 ^b |
| Mn ²⁺ | ⁶ S | -103.496685 | | |
| bipy | ¹ A _g | -81.427786 | 8.12 | 8.35 ^c |
| bipy ⁺ | ² B _g | -81.129222 | | |
| phen | ¹ A ₁ | -92.798075 | 7.96 | 8.30 ^c |
| phen ⁺ | ² B ₁ | -92.505586 | | |
| [Mn(bipy)] ⁺ | ⁷ A ₁ | -185.629842 | 10.14 | |
| | ⁵ B ₁ | -185.597295 | | |
| [Mn(bipy)] ²⁺ | ⁶ A ₁ | -185.257219 | | |
| | ⁴ B ₂ | -185.196321 | | |
| [Mn(phen)] ⁺ | ⁷ A ₁ | -197.012564 | 10.03 | |
| | ⁵ B ₁ | -196.980234 | | |
| [Mn(phen)] ²⁺ | ⁶ A ₁ | -196.643888 | | |
| | ⁴ B ₂ | -196.579748 | | |
| [Mn(bipy)(phen)] ²⁺ | ⁶ A ₁ | -278.255133 | | |
| | ⁴ B | -278.201519 | | |

^a In addition, the following bond dissociation energies can be derived from the computed data (D_0 at 0 K): BDE(Mn²⁺-bipy) = 9.06 eV, BDE(phen-Mn²⁺) = 9.50 eV, BDE(phen-Mn²⁺-bipy) = 4.99 eV, BDE(phen-Mn⁺-bipy) = 5.44 eV, BDE(Mn⁺-bipy) = 3.21 eV, and BDE(phen-Mn⁺) = 3.54 eV. ^b Reference 31. ^c Taken from: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. Gas-Phase Ion and Neutral Thermochemistry. *J. Phys. Chem. Ref. Data* **1988**, 17 (Suppl. 1).

The monocations [Mn(bipy)]⁺ and [Mn(phen)]⁺ are bound by 3.21 and 3.54 eV with respect to Mn⁺(⁷S) + L. In marked

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contrast, the dications [Mn(bipy)]²⁺ and [Mn(phen)]²⁺ are bound much stronger (9.06 and 9.50 eV, respectively) relative to the Mn²⁺(⁶S) + L asymptote. The larger bond strengths of the dicationic complexes can be attributed to the synergistic operation of two effects: (i) the higher charge of the dication enforces electrostatic bonding and (ii) the ground-state configuration of Mn²⁺(⁶S, 4s⁰5d⁵) allows for a better approach of the ligand compared to Mn⁺(⁷S, 4s¹5d⁵) where the occupied 4s orbital is partially repulsive. This line of reasoning is further supported by the significantly shorter Mn–N distances in the MnL²⁺ complexes (~194 pm) compared to MnL⁺ (~223 pm), see parts a and b of Figure 4. The lower bond energies of the bipy complexes is attributed to the quite large reorganization energy of the bipy ligand (see above). As phen does not undergo such a reorganization, its complexes with Mn²⁺ are more stable in the gas phase compared to those of bipy. While one might expect that the different flexibility of phen and bipy also leads to significant entropic differences between the two ligands, the computed differential bond dissociation energies (Δ BDEs) for ligand losses from both the mono- and dicationic complexes discussed here differ by less than 0.025 eV between H_{0K} , H_{298K} , and G_{298K} . However, the differences between phen and bipy level off if the bond strengths of the hypothetical planar cisoid bipy ligand are compared. The energy needed for bipy to change from its transoid ground-state conformation **Ia** into the hypothetical cisoid form **Ib** amounts to 0.33 eV, which matches the difference in bond energies of the monocation complexes MnL⁺; for the MnL²⁺ species, the difference is reduced from 0.44 to 0.13 eV. The dications [Mn(bipy)]²⁺ and [Mn(phen)]²⁺ are thermochemically stable toward Coulombic explosion by 1.19 and 1.47 eV, respectively, according to the DFT calculations. The stability with respect to charge separation can be attributed to the fact that the charge is partly delocalized among the respective arene ligand. In addition, the kinetic stability of the dication complexes MnL²⁺ is expected to be supported because of a sizable barrier imposed by Coulombic repulsion of the cationic fragments formed in the course of a charge-separation process.

The bisligated dication [Mn(bipy)(phen)]²⁺ has C_{2v} symmetry with a high-spin ground state (⁶A₁) and a quasi-tetrahedral coordination, that is, the ligands' planes are perpendicular to each other (Figure 4c). The bond dissociation energies of [Mn(bipy)(phen)]²⁺ are computed as 5.44 and 4.99 eV for losses of neutral phen or bipy, respectively, whereas the endothermicities of the charge-separation processes to afford phen⁺ and bipy⁺ amount to 3.26 and 3.08 eV, respectively. Hence, [Mn(bipy)(phen)]²⁺ is a thermochemically stable dication⁷¹ which is considerably stabilized by the two arene ligands. With the assumption that the competition of the various channels correlates with the energetics of the associated dissociation asymptotes, these results provide an explanation for the different branching ratios in the losses of neutral and monocationic ligands (Figure 5). Thus, the energy difference for the loss of a

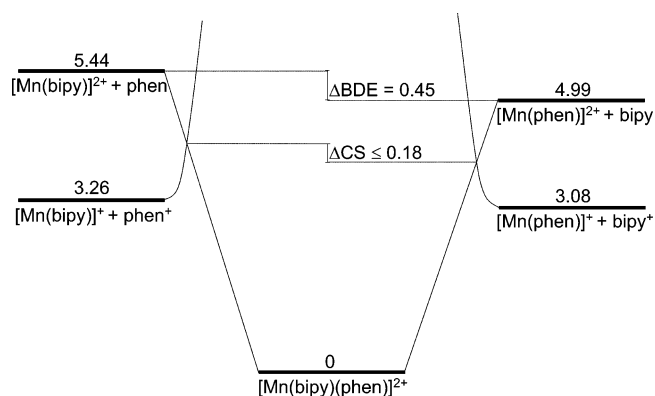


Figure 5. Simplified potential-energy surface for elimination of neutral ligands and charge separation for the bisligated dication [Mn(bipy)(phen)]²⁺, calculated at *mPW1PW91/DZP* level of theory. Relative energies are given in eV.

neutral ligand amounts to Δ BDE = 0.45 eV in favor of bipy, whereas that of the associated charge-separation asymptotes is only 0.18 eV. Provided that the differences in the asymptotes translate to the Coulombic barriers associated with charge separation, the difference between the energy barrier for elimination of neutral ligands is larger than that for charge separation, that is, Δ BDE > Δ CS (Figure 5). Further, it might be argued as well that the gain of conformational energy in the cis–trans rearrangement of bipy cannot fully be used in Coulombic explosion if electron transfer is the rate-determining step (see below).

In addition, some thermal ion–molecule reactions of the mixed dications [Mn(bipy)₂(phen)]²⁺, [Mn(bipy)(phen)₂]²⁺, and [Mn(bipy)(phen)]²⁺ with the monodentate ligand *N,N*-dimethylformamide (DMF) were performed. As demonstrated by Combariza and Vachet,^{72–74} the ion–molecule reactions of gaseous metal complexes with neutral ligand molecules can be used as a probe of the coordination structure. In the present context, we investigated whether the flexible bipy in some cases may act as a monodentate ligand and may hence be subject to ligand substitution. The reactions were performed in the hexapole under quasi-thermal conditions (E_{CM} nominally set to 0 eV) at DMF pressures which deliberately were high enough to allow multiple collisions and thus the occurrence of sequential ligand-exchange reactions. For the dications [Mn(bipy)₂(phen)]²⁺ and [Mn(bipy)(phen)₂]²⁺, neither products corresponding to displacement of bipy nor attachment of DMF or any other reactions are observed. This result is consistent with the view of these ions as complexes with octahedral coordination which prevents any attachment of an additional ligand,⁷² even for a strongly dipolar molecule such as DMF. In contrast, mass-selected [Mn(bipy)(phen)]²⁺ undergoes association of one DMF molecule to afford [Mn(bipy)(phen)(DMF)]²⁺ and then a second one to afford the putatively hexacoordinate complex [Mn(bipy)(phen)(DMF)₂]²⁺. Neither dications with

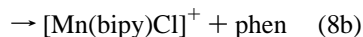
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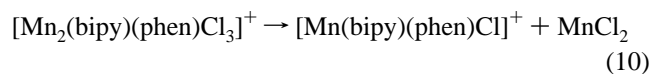
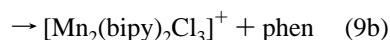
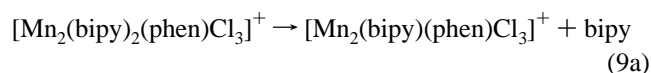
(74) Combariza, M. Y.; Vachet, R. W. *Anal. Chim. Acta* **2003**, *496*, 233–248.

larger number of DMF molecules nor substitution products, for example, $[\text{Mn}(\text{phen})(\text{DMF})_n]^{2+}$ were formed. These results indicate that despite its flexibility, bipy still acts as a chelating ligand.^{75,76} DMF is bonded to Mn^{2+} by 6.33 eV which is only more than half of the bond energy of $[\text{Mn}(\text{bipy})]^{2+}$ (9.06 eV) according to DFT calculations.

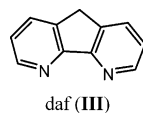


The monocation $[\text{Mn}(\text{bipy})(\text{phen})\text{Cl}]^+$ undergoes elimination of neutral bipy (reaction 8a) upon CID, yielding $[\text{Mn}(\text{phen})\text{Cl}]^+$ as a major product. Expulsion of phen (reaction 8b) to afford $[\text{Mn}(\text{bipy})\text{Cl}]^+$ is also observed, but the loss of bipy prevails at all of the collision energies investigated. This result confirms once more the stronger binding of phen to Mn^{II} . Upon CID of $[\text{Mn}(\text{bipy})(\text{phen})\text{Cl}]^+$, for example, the ratio between phen and bipy losses is about 1:20 at low collision energies, and even at $E_{\text{CM}} \approx 8$ eV, the two fragments $[\text{Mn}(\text{bipy})\text{Cl}]^+$ and $[\text{Mn}(\text{phen})\text{Cl}]^+$ corresponding to the evaporation of phen and bipy are formed in a ratio of ca. 1:4.

The chloro-bridged monocation $[\text{Mn}_2(\text{bipy})_2(\text{phen})\text{Cl}_3]^+$ undergoes elimination of bipy yielding the fragment $[\text{Mn}_2(\text{bipy})(\text{phen})\text{Cl}_3]^+$ (reaction 9a) as the major product, again revealing phen as a stronger ligand than bipy. Elimination of phen leading to a weak signal corresponding to $[\text{Mn}_2(\text{bipy})_2\text{Cl}_3]^+$ (reaction 9b) is observed only at increased collision energies. In addition, cluster degradation followed by elimination of MnCl_2 (reaction 11) takes place.



A similar behavior is found upon CID of mass-selected $[\text{Mn}_2(\text{bipy})(\text{phen})_2\text{Cl}_3]^+$ (data not shown), fully confirming the patterns for the “pure” and the mixed Mn^{II} complexes described above.



It is obvious that the “rigid” phen ligand has significantly greater chelation ability than the “flexible” bipy ligand according to the above results. For a further assessment of this conclusion, we intended to reduce the flexibility of bipy by bridging the two rings as realized in 4,5-diazafluorene (daf, structure III). This ligand is analogous to bipy but has a limited conformational flexibility and might therefore be

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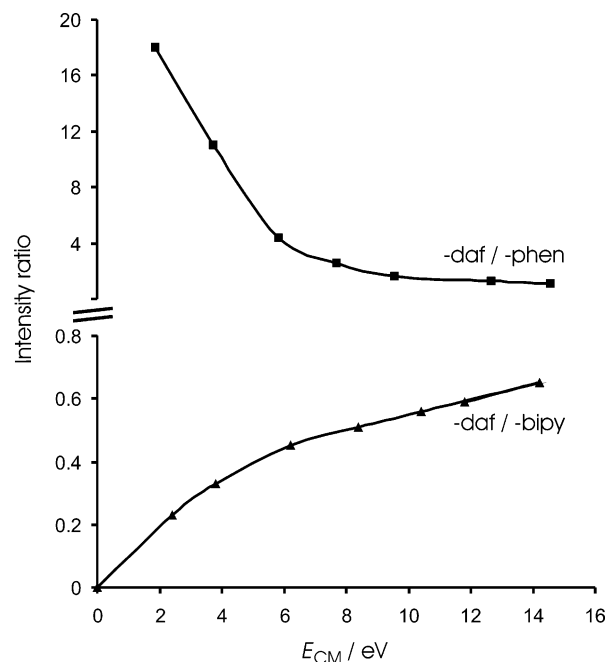


Figure 6. Ratios of the losses of daf vs phen as well as daf vs bipy upon CID of mass-selected $[\text{Mn}(\text{daf})(\text{phen})_2]^{2+}$ (■) and $[\text{Mn}(\text{daf})(\text{bipy})_2]^{2+}$ (▲), respectively, as a function of collision energy (E_{CM}).

expected to behave more similarly to phen. To a first approximation, daf may thus serve as a useful reference ligand to verify that the flexibility (or reorganization) of bipy is a decisive factor which reduces its effective coordination ability compared to that of phen. However, the fusion of the bipy skeleton with a five-membered ring distorts the central axis of the ligand in that the nitrogen atoms are expected to bear a larger distance than in bipy (cisoid form) and phen. Hence, daf is intuitively expected to be a somewhat weaker ligand than phen; in addition, the mere electrostatic interaction may be preferable for phen because of a simple size effect (see below).

As an experimental probe, CID experiments with the mixed-ligand complexes $[\text{Mn}(\text{daf})(\text{bipy})_2]^{2+}$ and $[\text{Mn}(\text{daf})(\text{phen})_2]^{2+}$ were performed, and the results are shown in Figure 6. CID of $[\text{Mn}(\text{daf})(\text{phen})_2]^{2+}$ reveals that despite a statistical discrimination the expulsion of daf is always favorable, while precisely the opposite behavior is observed for CID of $[\text{Mn}(\text{daf})(\text{bipy})_2]^{2+}$. These results demonstrate that daf has a complexation ability greater than that of bipy and lower than that of phen.

This conclusion is nicely confirmed by the CID spectra of the mixed trisligated complex $[\text{Mn}(\text{daf})(\text{bipy})(\text{phen})]^{2+}$ which show three different peaks resulting from detachments of bipy, daf, and phen, respectively (Figure 7). The relative intensities of the formed fragments clearly show that the trend for ligand dissociation diminishes in the order bipy > daf > phen, demonstrating that the complexation ability of the investigated ligands increases with opposite order, namely, the “rigid” phen is the most strongly bound ligand, whereas the “flexible” bipy is clearly the weakest, with daf occupying a position between them.

Finally, a more general aspect is to be addressed because there exists an alternative explanation for the observed trends

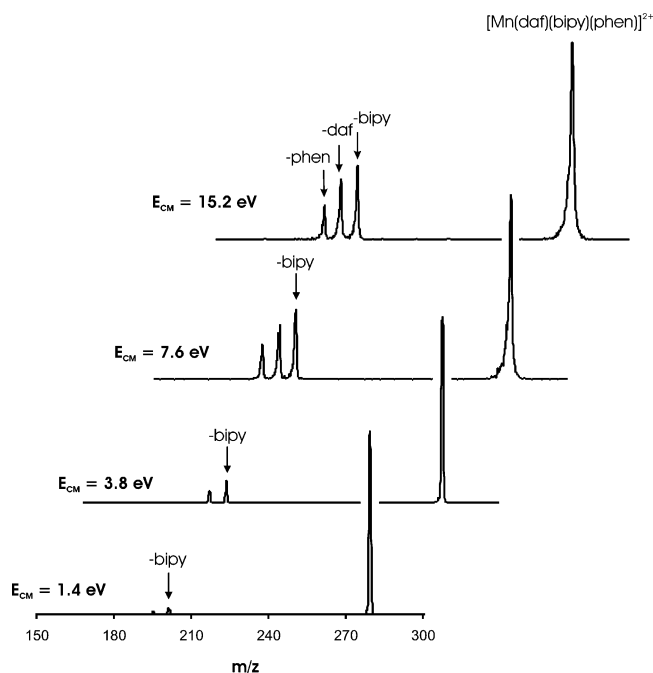


Figure 7. CID spectra of mass-selected $[Mn(daf)(bipy)(phen)]^{2+}$ at variable collision energies (E_{CM}). Signals corresponding to eliminations of bipy, daf, and phen from the trisligated Mn^{2+} complex are indicated by arrows.

in ligand binding. Thus, with increasing size, the polarizabilities of the ligands increase also, thereby enforcing the mere electrostatic interactions between the ligand and the metal cation. This line of reasoning would also predict that the bond strengths increase from bipy via daf to phen, as observed experimentally. Hence, it may be either the general electrostatic interaction or the ligands' flexibilities which determine the ligand order. To this end, we investigated a few alkylated derivatives of bipy and phen. In a comprehensive survey of several metal-ion complexes of main group and transition elements with pyridyl ligands, Satterfield and Brodbelt, *inter alia*, found that phenanthroline and dimethyl-bipyridines have more or less identical binding energies and attributed this finding to the similar polarizabilities of these ligands.⁷⁷ With respect to the current problem at hand, mixed complexes of phenanthroline and dimethyl-bipyridines may therefore allow the distinction between the two alternative explanations for the observed order of $bipy < phen$. Thus, the mono- and dicationic complexes $[Mn(bipy_{Me})(phen)Cl]^+$ and $[Mn(bipy_{Me})(phen)]^{2+}$, respectively, were investigated, where $bipy_{Me}$ stands for 5,5- as well as 6,6-dimethyl 2,2-bipyridine. Upon CID of the mass-selected complexes, both cations and dications, at moderate collision energies, loss of $bipy_{Me}$ is about 3 times favored over that of phen for the 5,5-isomer and even 4 times for the corresponding ions with 6,6-dimethyl 2,2-bipyridine. In contrast, the mixed complexes $[Mn(phen_{Me})(phen)Cl]^{2+}$ and $[Mn(phen_{Me})(phen)]^{2+}$, where $phen_{Me}$ stands for 4,7-dimethyl phenanthroline, show ratios of about 6:1 in favor of losing neutral phen which is a weaker ligand than the substituted $phen_{Me}$.⁷⁷ Likewise, the mixed complex $[Mn(bipy_{Me})(bipy)Cl]^+$ expels bipy upon CID with a preference in the order of 8:1; the mixed dicationic

complex $[Mn(bipy_{Me})(bipy)]^{2+}$ cannot be included here, because proton transfer from $bipy_{Me}$ to bipy prevails upon low-energy CID. We can conclude the following by resuming these results. For a mere effect of the ligands' polarizabilities, one would expect that phen and $bipy_{Me}$ have more or less identical binding abilities to Mn^{II} , as found by Satterfield and Brodbelt in the types of complexes these authors have studied. The significant difference between phen and $bipy_{Me}$ observed here therefore rather suggests that the flexibility of bipy ligands upon dissociation of the complexes determines the branching in the present case. The seeming contradiction between the previous findings of Satterfield and Brodbelt and the data reported here can, however, be attributed to the different types of complexes investigated, their bond strengths in particular. Thus, Satterfield and Brodbelt studied monocationic, bisligand complexes such as $M(L)_2^+$ for alkali and selected transition metals as well as trisligated dications of the type $M(L)_3^{2+}$, which have relatively low binding energies with regard to the loss of a single ligand. While the respective binding energies still exceed the energy required for the rotation around the central C–C bond in bipy,⁷⁷ the dissociation of these complexes may accordingly be subject to kinetic control, in that it initially leads to the cisoid conformation of the bipy fragment. If the total bond energies are larger, however, as in the bisligated Mn^{II} complexes investigated here (see footnote *a* of Table 1, for example), the conformational change of the bipy ligand is likely to occur prior to dissociation, thus resulting in a switch from kinetic to thermodynamic control.

Conclusions

Electrospray mass spectrometry in conjunction with density functional theory is successfully applied for the generation and characterization of coordination complexes of Mn^{II} with 1,10-phenanthroline, 2,2'-bipyridine, and 4,5-diazafluorene in the gas phase. In the present study, particular attention is paid to the competition between the different ligands. Collision-induced dissociation of Mn^{II} complexes with mixed ligands reveals that the expulsion of bipyridine is always favored compared to that of phenanthroline. By comparative studies of mixed ligand complexes including those with methylated derivatives, these observations can be attributed to the energetically preferred trans-conformation of the free bipyridine ligand, which phenanthroline cannot adopt.²⁵ Interestingly, the difference between phenanthroline and bipyridine becomes smaller when ligand loss is coupled with electron transfer in charge-separation reactions of bisligated Mn^{II} dications for both thermochemical as well as kinetic reasons. As expected, diazafluorene occupies an intermediate position between phenanthroline and bipyridine. The experimental findings, including the assignment of some of the Mn^{II} complexes as inherently thermochemically stable dications,⁷¹ are in good agreement with computational results derived from DFT calculations.

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