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Comparison of 2,2′-Bipyridine and 2,2′-Bipyridyl-*N*,*N*′-dioxide as Ligands in Zinc Complexes

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The complexation abilities of 2,2′-bipyridine (bipy) and 2,2′-bipyridyl-*N*,*N*′-dioxide (bipydiox) toward zinc(II) and the influence of these ligands on the properties and reactivities of the investigated complexes are compared by means of mass spectrometry, IR multiphoton dissociation spectroscopy, and theoretical calculations. The binding energy of bipydiox to zinc is slightly smaller than that of bipy, namely, by 0.1 eV in the mixed complex $[(\text{bipy})(\text{bipydiox})\text{ZnCl}]^+$. Accordingly, the differences in the properties and reactivities of the complexes of zinc(II)/bipydiox and zinc(II)/bipy are only minor. The mechanism of decarboxylation of $[(\text{L})\text{Zn}(\text{CH}_3\text{COO})]^+$ (L = bipy or bipydiox) is investigated in detail. The substantial difference between the ligands stems only from the possibility of oxygen transfer from bipydiox, which is here, however, observed only as a high-energy channel in the fragmentation of complexes $[(\text{bipydiox})\text{Zn}(\text{CH}_3\text{COO})]^+$.

Introduction

2,2′-Bipyridine (bipy) and its derivatives represent some of the most often used groups of ligands in organometallic chemistry.[1] Many molecules derived from a bisaryl skeleton bear an embedded axial chirality, which is a result of steric repulsion of hydrogen atoms or substituents in the ortho positions with respect to the connection of the two aryl moieties (Scheme 1). In the molecule of bipy, one of the ortho positions is occupied by a nitrogen atom and therefore does not bear any hydrogen atom or substituent. As a result, bipy is most stable in a coplanar arrangement of the pyridine rings and thus is not chiral (see Scheme 1). The particular arrangement of the nitrogen atoms, however, as well as the rigidity and chemical stability of the backbone makes bipy an extremely powerful ligand. In the interaction with a metal, one of the pyridine rings rotates so that both nitrogen atoms coordinate to a metal and the arrangement of the pyridine rings is again coplanar.[2] Chirality of the complexes can be achieved by the introduction some substituents to the bipy ligand, such that it becomes axially chiral,[3] or by a chiral arrangement of the bipy units in an octahedral fashion around the metal center.[4]

Oxidation of bipy leads to 2,2′-bipyridyl-*N*,*N*′-dioxide (bipydiox). The oxygen atoms prevent a coplanar arrangement of the aromatic rings, and therefore this compound is chiral and remains chiral also upon coordination to a metal (Scheme 1). The chiral induction by various derivatives and analogues of pyridine-*N*-oxide is of great success in organocatalysis, where these compounds serve as Lewis bases.[5,6] Here, we want to show the potential of bipydiox as an auxiliary for transition metals,[7] and zinc is chosen as a representative metal. The effects of bipydiox and bipy on the reactivities of zinc complexes are compared.

Experimental and Computational Details

The collision-induced dissociation (CID) experiments were performed with a TSQ Classic mass spectrometer with a QOQ configuration (Q stands for quadrupole and O stands for octopole) described in detail elsewhere.[8] The ions of interest were generated by electrospray ionization (ESI) from either an acetone solution of ZnSO_4 and a ligand or a methanolic

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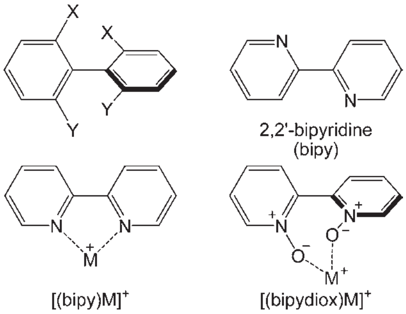
Scheme 1. Axial Chirality of a Bisaryl Compound (X, Y = H or any substituent) and Structures of bipy and Complexes of a Metal with bipy and bipydiox



solution of $Zn(CH_3COO)_2$ and a ligand, where the ligand was either 2,2′-bipyridine (bipy) or 2,2′-bipyridyl-*N*,*N*′-dioxide (bipydiox). The first quadrupole was used to record source spectra or to mass-select the desired ions. The mass-selected ions were collided with xenon ($p_{\mathrm{Xe}} \cong 0.08$ mTorr; 80% transmission of the parent ions at $E_{\mathrm{LAB}} = 30$ eV) in the octopole collision cell, and the fragments were analyzed by Q2. Further decreasing of the collision-gas pressure did not influence the determined cross sections. The collision energy was varied by changing the potential offset between Q1 and O. The nominal zero collision energy was determined by the retarding potential analysis (see the Supporting Information, SI), and the energy resolution was 1.2 ± 0.1 eV (full width at half-maximum). The appearance energies (AEs) of various fragmentation channels can be determined from the dependence of their relative cross sections on the collision energy.[9−11] The relative cross sections were evaluated using the L-CID program,[9] which simulates the data based on the electrostatic theory,[12] statistical rate theory,[13] and RRKM theory.[14] The simulation requires only input on the parent ion (the kinetic-energy resolution, the number of degrees of freedom, and the number of free rotors, i.e., single bonds with free rotations) and information on whether the transition state for the dissociation is loose or tight. It is assumed that the parent ions are thermalized; our experimental setup, however, does not allow thermalization, which results in a systematic underdetermination of the binding or activation energies.[15] In the systematic investigation of the fragmentation of $[Cu(PhO)(L)]^+$, where PhO stands for the phenoxy ligand and L stands for water, methanol, tetrahydrofuran, thiophene, ammonia, pyrrole, imidazole, pyridine, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, and 1,2-dimethoxyethylene, we have encountered an average error of −0.2 eV with respect to the theoretical calculations at the B3LYP/TZVP level.[15] The experimental data were obtained in two independent measurements, and each result was fitted two times with the L-CID program. The results and parameters used for the fitting are given in detail in the SI.

The gas-phase IR spectra of mass-selected ions were recorded using a Bruker Esquire 3000 ion trap mounted to a free electron laser (FEL) at CLIO (Centre Laser Infrarouge d'Orsay, Orsay, France).[16] The FEL was operated in the 40−45 MeV electron-energy range, and it provided light in the 1000−1800 cm^{-1} range. The relative spectral line width of the FEL is about 1%, and the precision of the measurement of the wavenumbers with a monochromator is about 1 cm^{-1}. The experimental dispersion in the measurement of the wavenumbers was minimized by averaging of 32 measurements for each point in a raw spectrum. The ions were generated by the ESI as described above. The ions were mass-selected and stored in the ion trap. The fragmentation was induced by four laser macropulses of 8 μs admitted to the ion trap, and the dependence of the fragmentation intensities on the wavelength of the IR light gives the IR multiphoton dissociation (IRMPD) spectra. The power of the FEL slightly changes in depending on the wavenumbers (see the SI); the reported IRMPD spectra are averages of two raw spectra and are not corrected for the power of the FEL.

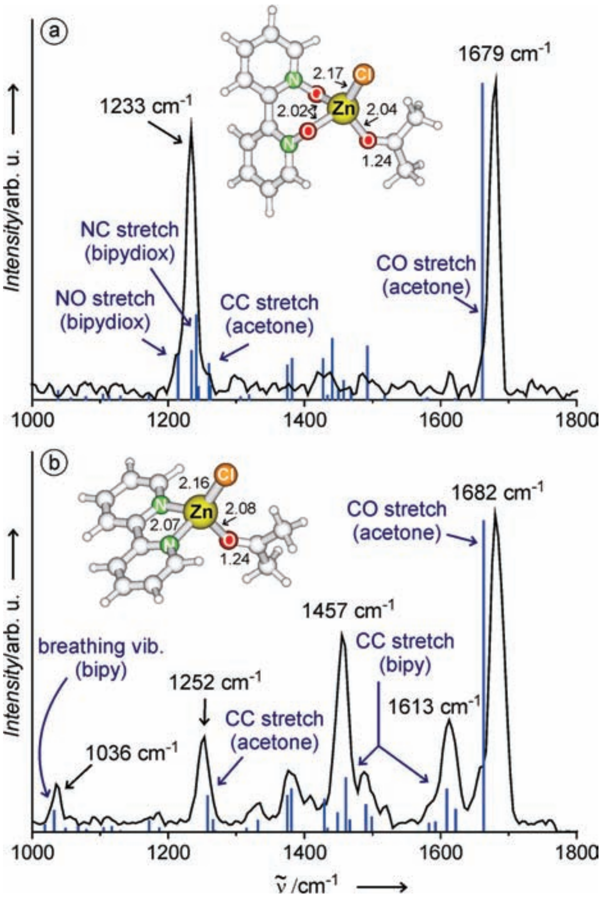


Figure 1. Experimental IRMPD spectra and theoretical IR spectra of $[(bipydiox)ZnCl(CH_3COCH_3)]^+$ (a) and $[(bipy)ZnCl(CH_3COCH_3)]^+$ (b), respectively. The insets show the optimized structures, with selected bond lengths given in angstroms.

The computational density functional theory (DFT) study was performed using B3LYP[17−20] together with the 6-311+G(2d,p) basis set, as implemented in the *Gaussian 03* package.[21] All minima and transition states were identified by analysis of the Hessian matrix. All energies given below refer to 0 K (the energies are sums of the total energies and zero-point vibrational energies). The calculated frequencies were

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Table 1. Theoretical Parameters of the [(L)ZnCl(CH_3COCH_3)]$^+$, [(L)Zn(CH_3COO)]$^+$, and [(L)Zn(CH_3)]$^+$ Complexes, Where L = bipy or bipydiox

			binding energy [eV]		
	ν_{CO} [cm^{-1}][a]	R_{CO} [Å]	CH_3COCH_3	CH_3COO	.
CH_3COCH_3	1780	1.210			
[ZnCl(CH_3COCH_3)]$^+$	1625	1.255	3.26		
[(bipydiox)ZnCl(CH_3COCH_3)]$^+$	1687	1.237	1.05		3.15
[(bipy)ZnCl(CH_3COCH_3)]$^+$	1689	1.236	0.97		2.98
[(bipydiox)Zn(CH_3COO)]$^+$	1462 (s)[b]	2.015		3.49	
	1528 (a)[c]	2.018			
[(bipy)Zn(CH_3COO)]$^+$	1461 (s)[b]	2.016		3.62	
	1526 (a)[c]				

[a] Not scaled. [b] s = symmetric. [c] a = antisymmetric.

scaled by a factor of 0.985,[22] which leads to the overall best agreement between the theory and experiment using a single scaling factor for all spectra studied here (compare below).[23] Using this factor, the stretching mode of the carbonyl group of acetone in complexes [(L)ZnCl(CH_3COCH_3)]$^+$, where L = bipy or bipydiox, and the N−O stretching mode of the zinc-coordinated bipydiox are predicted at slightly lower wavenumbers than those found experimentally (cf. Figure 1a). The agreement can be improved by using an individual scaling factor of 0.996.[24] We, however, prefer to use a uniform scaling. We note in passing that it has been reported for other systems that the stretching frequencies of the bonds directly neighboring a metal are predicted at slightly lower wavenumbers using the B3LYP method.[25] All optimized structures and their energies are given in the SI.

Results and Discussion

The effect of the ligands is first investigated in their complexes, [(bipy)ZnCl(CH_3COCH_3)]$^+$ and [(bipydiox)ZnCl(CH_3COCH_3)]$^+$, with zinc chloride and acetone. The structure and properties of the complexes are investigated by means of IRMPD spectroscopy and DFT calculations. The idea is to use the carbonyl stretching mode of acetone as a marker of the electronic properties of the complexes. Recently, we have shown on complexes of copper that the binding energies of ligands are closely correlated with their ability to share electrons with the metal.[15] Here, it is to be expected that a stronger-bound ligand will share a larger electron density with the zinc ion and thereby affect also the binding between zinc and acetone. The stronger the binding between zinc and acetone, the larger the red shift in the CO stretching that should be observed.

IRMPD spectroscopy is based on the mass spectrometric detection of fragments formed upon absorption of IR photons by the parent ions isolated in the gas phase. The dependence of the fragmentation yield on the wavelength of the IR photons thus reflects the IR spectrum. The clear advantage of this technique is a high sensitivity because, in principle, even fragmentation of just a few molecules can be detected. On the other hand, IRMPD spectroscopy has a multiphotonic character, which means that the intensities of the peaks in the spectrum do not correlate exactly with those in the conventional IR spectrum. Moreover, the number of photons necessary for induction of the dissociation can differ with the wavelength. Hence, in IRMPD spectra, more weight is given to the positions of the bands than to their intensities.[26−28]

The IRMPD spectrum of [(bipydiox)ZnCl(CH_3COCH_3)]$^+$ is dominated by two bands at 1679 and 1233 cm^{-1}, respectively (Figure 1a). A comparison with the calculated spectrum reveals that these peaks correspond to the stretching of the carbonyl group and to the stretching of the NO groups of bipydiox, respectively. Similarly, the largest peak in the IRMPD spectrum of [(bipy)ZnCl(CH_3COCH_3)]$^+$ corresponds to the carbonyl stretching mode (Figure 1b). The remaining peaks in the spectrum come mainly from the vibrations of the bipy ligand.[29]

The calculated wavenumber for the CO vibration in isolated acetone amounts to 1780 cm^{-1} (Table 1). The coordination of acetone to ZnCl$^+$ results in a red shift of the CO vibration to 1625 cm^{-1} because of participation of the π electrons of the CO bond in the bonding to zinc. Accordingly, also the CO bond length is elongated from 1.210 Å in isolated acetone to 1.255 Å in the [ZnCl(CH_3COCH_3)]$^+$ complex. Coordination of the bipydiox ligand to [ZnCl(CH_3COCH_3)]$^+$ results in a substantial electron density transfer from the incoming ligand to the remaining part of the complex. According to the Mulliken population analysis, a positive charge of 0.67 e is built up on the bipydiox ligand. The changed electron distribution in the complex leads to the reduction of the binding energy between acetone and zinc and accordingly the CO vibration is blue-shifted to 1687 cm^{-1} (not scaled, Table 1) and the CO bond length is reduced to 1.237 Å compared to the values for [ZnCl(CH_3COCH_3)]$^+$.

In agreement with the experiment, the effect of bipy on the binding and properties of acetone in the complex [(bipy)ZnCl(CH_3COCH_3)]$^+$ is almost identical with the effect of bipydiox in [(bipydiox)ZnCl(CH_3COCH_3)]$^+$. The CO stretching mode is located at 1689 cm^{-1} (not scaled, Table 1), and the CO bond length is 1.236 Å.

The relative binding energies of bipydiox and bipy toward zinc are investigated by the CID of the zinc complex [(bipy)(bipydiox)ZnCl]$^+$ containing both ligands. The dissociation of [(bipy)(bipydiox)ZnCl]$^+$ leads exclusively to the loss of

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[29] During measurements of the IRMPD spectra of [(bipydiox)ZnCl(CH_3COCH_3)]$^+$ (Figure 1a), an attenuator of the laser power was used in order to prevent saturation during the fragmentations upon irradiation at the bands at 1233 and 1679 cm^{-1}. This can be a reason for the missing bands of the aromatic skeleton in the range 1350−1500 cm^{-1}.

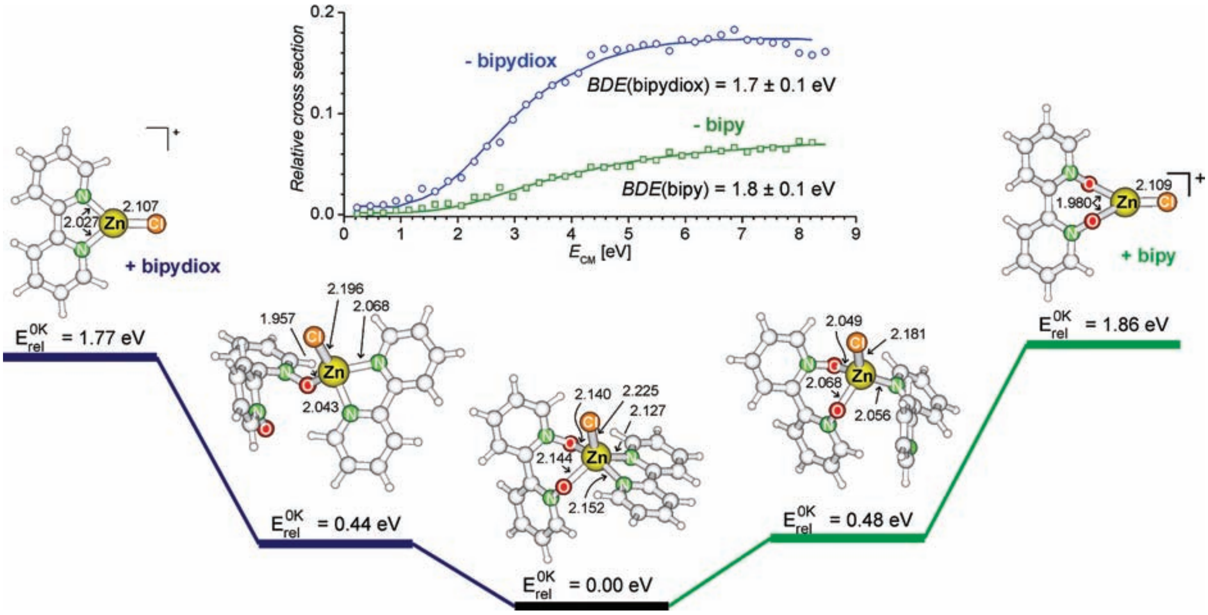

Figure 2. Minima along the B3LYP/6-311+G(2d,p) potential-energy surface for the dissociation of $[(\text{bipy})(\text{bipydiox})\text{ZnCl}]^+$. The energies are given at 0 K relative to $E^{0\text{ K}} = -3380.621\,211$ hartree. Selected bond lengths are given in angstroms. The inset shows energy-resolved CID (open symbols). The solid lines correspond to fits of the relative cross sections for the losses of bipydiox and bipy, respectively, by the L-CID program. The fitting leads to the experimental bond dissociation energies of 1.7 ± 0.1 and 1.8 ± 0.1 eV for the loss of bipydiox and bipy, respectively.

either bipydiox or bipy. The former is more abundant, which suggests that the binding energy of bipydiox is smaller than that of bipy. In order to estimate the binding energies from the energy-dependent relative cross sections, we have used the fitting program L-CID by Chen and co-workers.[9] Assuming loose transition states for the eliminations of bipydiox and bipy, respectively, we arrive at values of 1.7 ± 0.1 and 1.8 ± 0.1 eV, respectively, by a simultaneous fitting of both channels (Figure 2).

The complementary DFT calculations show that the eliminations of the ligands proceed via high-energy-lying isomers, in which one of the ligands is monodentate.[2] Such a rearrangement of bipydiox leads to an increase of the energy of the complex by 0.44 eV, and the rearrangement of bipy raises the energy by 0.48 eV. The elimination of bipydiox requires 1.77 eV, whereas the elimination of bipy requires 1.86 eV, which is in excellent agreement with the experimental values. The results thus show that the binding energy of the zinc−bipy bond is slightly larger than that of the zinc−bipydiox bond, which corresponds well with the above conclusion that bipy has a larger impact on the zinc/acetone complex. We note in passing that the transition-state structures for the eliminations of bipy and bipydiox, respectively, were not determined and instead continuous endothermic barrierless dissociations were considered.

The effect of bipy and its oxidized variant on the zinc complexes is further demonstrated by a comparison of the reactivities of $[(\text{L})\text{Zn}(\text{CH}_3\text{COO})]^+$, where L is either bipy or bipydiox. The complexes of interest can be generated by ESI from a methanolic solution of zinc acetate and one of the ligands. The structure of the complexes is first investigated by means of IRMPD spectroscopy. The spectra of both complexes, $[(\text{bipydiox})\text{Zn}(\text{CH}_3\text{COO})]^+$ and $[(\text{bipy})\text{Zn}(\text{CH}_3\text{COO})]^+$, are dominated by peaks at roughly 1460 cm^{-1}, which suggests that the acetate ion is coordinated as a bidentate ligand in both complexes.[30] In the case of monodentate coordination of acetate, an intense band above 1600 cm^{-1} corresponding to the stretching mode of the uncoordinated carbonyl function would be expected. A comparison of the experimental spectra with the theoretical spectra fully supports this conclusion. Thus, the theoretical spectra for the complexes with monodentate acetate (Figure 3b,d) show that the CO vibration bands should appear at roughly 1200 and 1770 cm^{-1}, which is not reflected in the experimental spectra. Instead, a nice agreement between the experimental spectra and the theoretical spectra for the isomers bearing bidentate acetate is observed (Figure 3a,c). The dominant peaks in the spectra reflect the symmetric and antisymmetric stretching of the carboxyl group and the deformation vibrations of the methyl group. In addition, the spectrum of $[(\text{bipydiox})\text{Zn}(\text{CH}_3\text{COO})]^+$ contains a second band at 1225 cm^{-1}, which corresponds to the N−O stretching modes of the bipydiox ligand.

Investigation of the unimolecular reactivity reveals that both complexes undergo a facile loss of CO_2 to form $[(\text{L})\text{Zn}(\text{CH}_3)]^+$ (Figure 4).[31] Other fragmentation channels substantially differ, however. For the $[(\text{bipy})\text{Zn}(\text{CH}_3\text{COO})]^+$ complex, the loss of CO_2 is followed by a loss of the entire acetoxy group (Figure 4b). Note that either acetoxy radical can be eliminated or CO_2 and the methyl radical can be lost in two subsequent steps (we will use $[\text{CH}_3,\text{CO}_2]^\bullet$ notation in the following). The L-CID simultaneous fitting of the energy-dependent fragmentation cross sections of both losses provides the threshold energies $E_0(\text{CO}_2) = 1.7 \pm 0.1$ eV[32] and $E_0([\text{CH}_3,\text{CO}_2]^\bullet) = 2.5 \pm 0.1$ eV.[33]

The reactivity of $[(\text{bipydiox})\text{Zn}(\text{CH}_3\text{COO})]^+$ is dominated by the loss of CO_2. Elimination of the $[\text{CH}_3,\text{CO}_2]^\bullet$ radical is almost completely suppressed in that only negligible signals for this fragmentation channel occur at the largest collision

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(32) A tight transition state was assumed.

(33) A loose transition state was assumed.

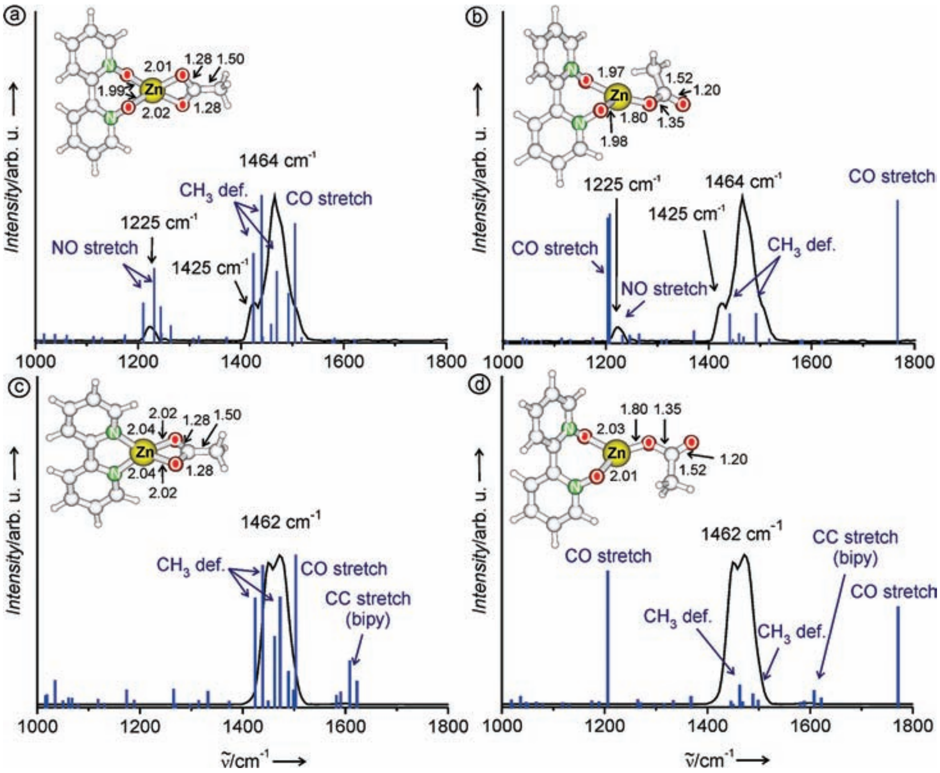

Figure 3. IRMPD spectra of $[(bipydiox)Zn(CH_3COO)]^+$ and $[(bipy)Zn(CH_3COO)]^+$ compared with the theoretical spectra of isomers with bidentate acetate (parts a and c, respectively) and with monodentate acetate (parts b and d, respectively). The insets show the optimized structures of the isomers with selected bond lengths given in angstroms.

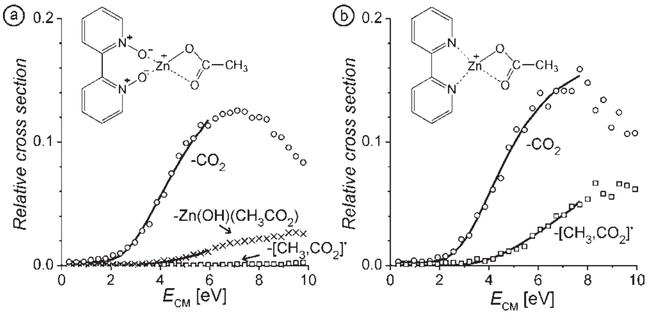

Figure 4. Energy-resolved CID of $[(bipydiox)Zn(CH_3COO)]^+$ (a) and $[(bipy)Zn(CH_3COO)]^+$ (b). The experimental data are given as points. The solid lines show the L-CID fits of the data.

energies studied (Figure 4a). Instead, elimination of CO_2 is in competition with a loss of $[Zn(OH)(CH_3COO)]$. The fitted threshold energies for these two channels amount to $E_0(CO_2) = 1.7 \pm 0.1$ eV[32] and $E_0[Zn(OH)(CH_3COO)] = 2.1 \pm 0.1$ eV (a simultaneous fitting of both channels was performed).[32]

The computational investigation of the CO_2 loss shows very similar results for both complexes (Figure 5). The reaction starts with a rearrangement of acetate from the bidentate binding mode to the monodentate binding. In the next step, the methyl group approaches the zinc ion and at the same time the Zn−O bond is cleaved. The rearrangement proceeds without inversion of the configuration of the methyl group, and the associated barrier heights are 2.14 eV for $[(bipy)Zn(CH_3COO)]^+$ and 2.10 eV for $[(bipydiox)Zn(CH_3COO)]^+$. The calculated energy barriers are slightly higher than the values obtained experimentally, which can be explained by the fact that the ions are not thermalized in our triple−quadrupole setup.[34] Alternatively, if the L-CID fitting of the experimental data is performed with the condition of "loose"

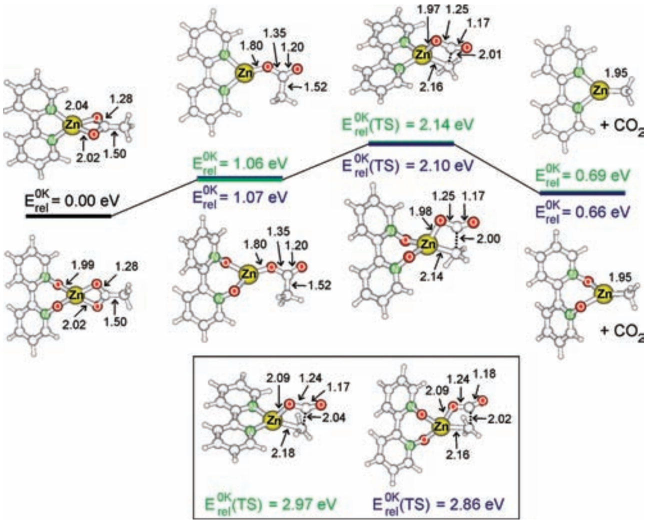

Figure 5. Minima and transition states (denoted by TS) along the B3LYP/6-311+G(2d,p) potential-energy surface for the elimination of CO_2 from $[(bipydiox)Zn(CH_3COO)]^+$ (in blue) and from $[(bipy)Zn(CH_3COO)]^+$ (in green). The energies are given at 0 K relative to $E^{0\ K}([(bipydiox)Zn(CH_3COO)]^+) = -2653.466293$ hartree and $E^{0\ K}([(bipy)Zn(CH_3COO)]^+) = -2503.100705$ hartree, respectively. The selected bond lengths are given in angstroms. The inset shows alternative transition-state structures with configuration inversion of the methyl group.

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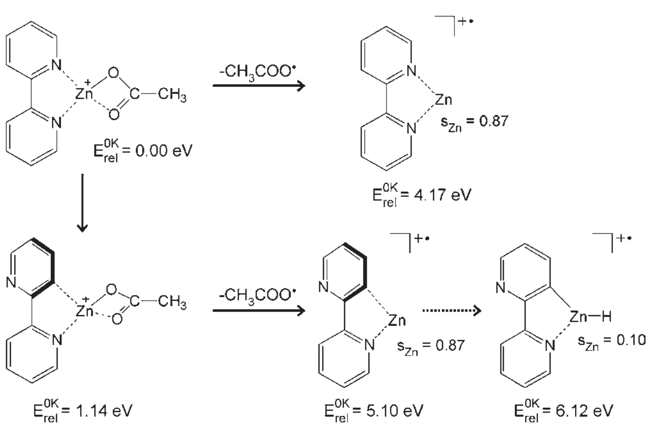
Scheme 2. Elimination of the Acetoxy Radical from $[(\text{bipy})\text{Zn}(\text{CH}_3\text{COO})]^{+a}$

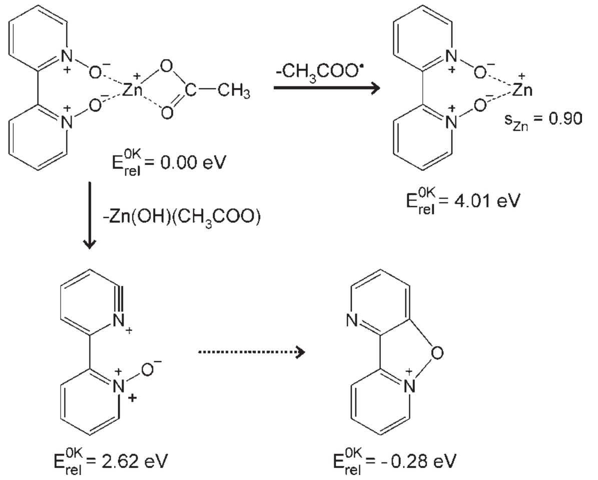


[a] Energies are given relative to $E^{0\text{ K}}([(\text{bipy})\text{Zn}(\text{CH}_3\text{COO})]^+)$; s_{Zn} denotes a spin localization at zinc determined by Mulliken population analysis. If the stepwise elimination of CO_2 and $\text{CH}_3^\bullet$ is considered, then all energies drop by 0.58 eV (except $E_{\text{rel}}{}^{0\text{ K}} = 0.00$ eV).

transition states, we obtain experimental barrier heights of 2.2 ± 0.1 eV for $[(\text{bipy})\text{Zn}(\text{CH}_3\text{COO})]^+$ and 2.1 ± 0.1 eV for $[(\text{bipydiox})\text{Zn}(\text{CH}_3\text{COO})]^+$, which is in perfect agreement with the theory (see the SI). We note in passing that also transition-state structures for the methyl rearrangement with inversion of the configuration can be found (inset in Figure 5), but these structures correspond to much higher energy barriers (2.97 eV for $[(\text{bipy})\text{Zn}(\text{CH}_3\text{COO})]^+$ and 2.86 eV for $[(\text{bipydiox})\text{Zn}(\text{CH}_3\text{COO})]^+$).

Decarboxylation of the $[(\text{bipy})\text{Zn}(\text{CH}_3\text{COO})]^+$ complex can be followed by the loss of the methyl group. This stepwise elimination of the acetoxy group requires an energy of 3.58 eV. In comparison, the direct loss of the acetoxy radical is 4.17 eV endothermic.[35] Both energy demands, however, largely exceed the experimental threshold of the acetoxy loss evaluated as 2.5 ± 0.1 eV, which cannot be only explained by the high internal energy content of the ions formed by the ESI. As an alternative mechanism, we have considered fragmentation pathways involving a "rollover" cyclometalation of bipy,[36] but these pathways lay more than 1 eV higher in energy than a simple cleavage of the acetoxy ligand (Scheme 2). In addition, we have probed the fragmentation of the $[(\text{phen})\text{Zn}(\text{CH}_3\text{COO})]^+$ complex, where phen is 1,10-phenanthroline, and therefore the possible "rollover" cyclometalation is switched off. The fragmentation of $[(\text{phen})\text{Zn}(\text{CH}_3\text{COO})]^+$ again shows losses of CO_2 and the acetoxy group as dominant channels with threshold energies of 1.6 ± 0.1 and 2.7 ± 0.1 eV, respectively (for spectra and L-CID simulations, see the SI). These results are thus very similar to the results found for $[(\text{bipy})\text{Zn}(\text{CH}_3\text{COO})]^+$, and therefore the mechanism most probably corresponds to a stepwise or direct loss of the acetoxy group associated with the formation of a zinc(I) ion.

Scheme 3. Elimination of the Acetoxy Radical and $[\text{Zn}(\text{OH})(\text{CH}_3\text{COO})]$ from $[(\text{bipydiox})\text{Zn}(\text{CH}_3\text{COO})]^{+a}$



[a] Energies are given relative to $E^{0\text{ K}}([(\text{bipydiox})\text{Zn}(\text{CH}_3\text{COO})]^+)$; s_{Zn} denotes a spin localization at zinc determined by Mulliken population analysis.

The fragmentation of the $[(\text{bipydiox})\text{Zn}(\text{CH}_3\text{COO})]^+$ complex might, in principle, again proceed with an analogous mechanism. The calculations suggest that direct cleavage of the acetoxy radical requires 4.01 eV, and the subsequent elimination of CO_2 and the methyl radical is 3.42 eV endothermic. The fact that we almost do not observe this channel in the fragmentation of the $[(\text{bipydiox})\text{Zn}(\text{CH}_3\text{COO})]^+$ complex is thus primarily based on the reactivity of bipydiox. *N*-Oxide compounds can serve as efficient oxidants by transferring an oxygen atom to a reaction partner. At high internal energies, a hydroxyl group can be transferred from bipydiox to the zinc ion, thereby forming zinc (hydroxide) acetate. The simplest fragmentation leading to 2-(6-dehydropyridin-2-yl)pyridine-*N*-oxide and zinc (hydroxide) acetate is 2.62 eV endothermic, which is thus well below the energy demand for the loss of the acetoxy group (Scheme 3). A possible rearrangement of 2-(6-dehydropyridin-2-yl)pyridine-*N*-oxide to a more stable tricyclic product (see Scheme 3) makes the overall fragmentation even exothermic.

The oxygen-transfer reaction from a ligand based on the bipydiox skeleton to a metal represents an undesired reactivity if the bipydiox derivative is used as a chiral auxiliary. The reactivity studied here, i.e., the zinc-assisted decarboxylation of acetate, proceeds, however, much more efficiently than the oxygen transfer, and the oxygen transfer occurs only when an unfavored compound of zinc(I) should be formed. Presumably, the oxygen-transfer reaction could always interfere in reactions that involve a low-valence state of a given metal. On the other hand, the oxygen transfer can also represent a desired mode of reactivity, which even broadens the scope of possible applications of ligands based on bipydiox.[37,38]

Conclusions

We have demonstrated that bipydiox has complexation properties very similar to those of the commonly used ligand bipy. For complexes $[(\text{L})\text{ZnCl}(\text{CH}_3\text{COCH}_3)]^+$, where L is either bipydiox or bipy, it is shown that the interaction of zinc

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with acetone is only slightly influenced upon a change of the ligand L. The strength of the interaction between zinc and acetone is assessed by the measurement of the stretching mode of the carbonyl group of acetone. Upon a change of the ligand from bipy to bipydiox, the CO mode is only 3 cm^{-1} red-shifted. This suggests that the zinc–acetone interaction is slightly stronger if bipydiox is used as the ligand, but the experimental differences are negligible.

The relative binding energies of bipydiox and bipy are determined from the fragmentation of the complexes $[(\mathrm{bipy})(\mathrm{bipydiox})\mathrm{ZnCl}]^+$. The results show that bipy is a stronger bound ligand, but the difference between the binding energies of bipy and bipydiox is only 0.1 eV.

Finally, we have also investigated reactions occurring at the zinc ion complexed by either bipy or bipydiox. Complexes $[(\mathrm{L})\mathrm{Zn}(\mathrm{CH_3COO})]^+$ undergo a rearrangement followed by a loss of CO_2. The reactions proceed on equivalent potential-energy surfaces in that the experimental appearance energies for the CO_2 losses from both complexes are equal, and the theory predicts only a 0.04 eV energy difference in the corresponding activation barriers. The reactivities of $[(\mathrm{L})\mathrm{Zn}(\mathrm{CH_3COO})]^+$ show also a potential drawback of using derivatives of bipydiox as chiral auxiliaries: We observe an oxygen transfer from the ligand to zinc as a high-energy channel in the unimolecular fragmentation of $[(\mathrm{bipydiox})\mathrm{Zn}(\mathrm{CH_3COO})]^+$. In the present case, this channel is disfavored, but it might play an important role in complexes of low-valence metals.

The results thus indicate that derivatives of bipydiox can be applied (without major reactivity perturbations) as chiral auxiliaries in reactions, where usually achiral ligands based on the bipy skeleton are used. The limitations stem only from the possible oxidation activity of the ligands based on the bipydiox skeleton in that low-valence metals can be oxidized.[38]

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Supporting Information Available: Total energies, optimized geometries, and the dependence of the FEL intensity on the wavenumbers during measurements. This material is available free of charge via the Internet at http://pubs.acs.org.