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Electrospray Ionization Tandem Mass Spectrometry of Polymetallic μ-Oxo- and Carboxylate-Bridged $[Ru_3O(CH_3COO)_6(Py)_2(L)]^+$ Complexes: Intrinsic Ligand (L) Affinities with Direct Access to Steric Effects

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$[Ru_3O(CH_3COO)_6(py)_2(L)]^+$ ($\mathbf{1}^+$) are polymetallic singly charged cationic complexes with a unique structural arrangement in which three neutral ligands are bound via ruthenium atoms to a highly delocalized symmetrical triangular tridentate $[Ru_3O(CH_3COO)_6]^+$ core bonded by a μ-oxo and six carboxylate bridges. Several $\mathbf{1}(PF_6)$ complexes with various terminal ligands (L) and two pyridines (py) used as reference ligands were synthesized. These complexes were directly transferred from a methanol solution to the gas phase and characterized by electrospray ionization mass spectrometry (ESI-MS) and subsequently dissociated by gentle collisions with argon molecules via ESI-MS/MS. The applicability of Cooks' kinetic method (CKM) to rank the binding affinities of a set of L to the $[Ru_3O(CH_3COO)_6]^+$ core was demonstrated by the good linear correlation ($R = 0.98$) observed in a CKM plot for which the relative peak intensities of the two fragment ions arising from the competitive loss of py or L as well as L affinities predicted by PM3(tm) calculations were used. Steric effects greatly affect L affinities, as evidenced by the values measured for *ortho*-substituted pyridines. The gaseous $\mathbf{1}^+$ were found to display a relatively high effective temperature of 1258 K. We have therefore extended CKM to investigate metal−ligand interactions, showing its usefulness to order and measure intrinsic (no solvent or counterion effects) ligand affinities to large and structurally intricate polymetallic complexes.

Introduction

Trinuclear complexes of general formula $[M_3O(RCOO)_6(L)_3]^n$ (where M = transition metal, R = alkyl or aryl groups, and L = solvent or N-heterocyclic ligand, $n = 1-$ to $3+$) are unique since they possess a symmetrical triangular structure in which the metal ions are held together by a μ-oxo and six carboxylate bridges.[1] Triruthenium compounds are particularly interesting owing to the strong electronic interaction among the ruthenium ions that gives rise to a totally delocalized $[Ru_3O]^+$ core, which thus behaves as a single metal center. $[Ru_3O]^+$ constitutes also an electroactive core with up to five reversible redox processes in the range of −1.5 to 2.5 V (vs SHE), whose potentials can be modulated by changing the terminal and bridging ligands.[2] Each monoelectronic redox process is accompanied by drastic chromatic changes[3] that provide suitable and attractive combinations of electrochemical stimuli and spectroscopic response.

The $[Ru_3O]^+$ core is also an important building block used to construct several supramolecular structures.[4] Therefore, techniques able to provide metal−ligand strengths and structural characterization of both the building blocks and supramolecular assemblies are highly valuable. Usually, this characterization is performed by X-ray and NMR spectroscopy, but we showed recently that electrospray ionization mass spectrometry (ESI-MS) and its tandem version (ESI-MS/MS) are also able to provide fine structural characterization of the doubly charged dimeric cation $[\{[Ru_3O]^+(CH_3COO)_6(py)_2\}_2(BPEB)]^{2+}$, where BPEB = *trans*-1,4-bis[2-(4-pyridyl)ethenyl]benzene.[5]

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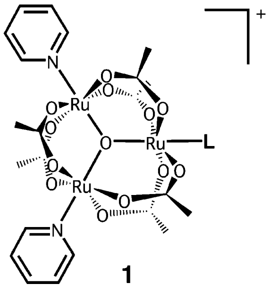
10.1021/om060026k CCC: $33.50

Scheme 1



ESI[6] has greatly expanded the applicability of mass spectrometry by making possible the gentle ionization of previously MS-untreatable molecules and ions, most particularly labile species with low thermal stability and high polarity or mass, or both. ESI-MS can easily handle such species including inorganic and organometallic salts[7] and even weakly bonded species such as neutral[8] or ionic[9] supramolecular assemblies. ESI-MS(/MS) has also been shown to be a powerful tool for the structural characterization of organometallic reaction intermediates[10] and for catalyst screening.[11]

We therefore realized that ESI-MS(/MS) could offer the unique opportunity to gently transfer a variety of $[Ru_3O(CH_3COO)_6(L')_2(L)]^+$ ($\mathbf{1}^+$) complexes directly from solution to the gas phase so as to order (and eventually measure) their intrinsic (solvent- and counterion-free) properties. Herein we report results from ESI-MS/MS experiments that allowed us to sample and gently dissociate a series of gaseous $\mathbf{1}^+$ and evaluate, for the first time, the relative binding strengths (affinities) of the terminal L to the unique $[Ru_3O(CH_3COO)_6]^+$ core. Using values from PM3(tm) calculations as reference, the reliability of Cooks' kinetic method (see below) to order and measure these L affinities was also evaluated.

Experimental Section

Except for the aqua complex ($L = H_2O$), where the anion was Cl^-, complexes $\mathbf{1}^+$ were prepared as PF_6^- salts with L = NO, 1,3-(bispyridyl)propane (BPP**)**, 1,2-bispyridylethylene (BPE), vinylpyridine (vpy), 4-ethylpyridine (4Etpy), pyridine (py), 2-ethylpyridine (2-Etpy), 4,4′-bipyridine (4,4′-bpy), pyrazine (pz), dimethylsulfoxide (DMSO), 2-chloropyridine (2-Clpy), CH_3OH, and CH_3CN (Scheme 1). These salts were synthesized following a general procedure described elsewhere.[12] Typically, 1 mmol of L was added to 0.1 mmol of $[Ru_3O(CH_3COO)_6(py)_2(CH_3OH)]PF_6$ dissolved in 25 mL of CH_2Cl_2. The mixture was poured into diethyl ether after 20 h reaction at room temperature. The dark precipitate was filtered, washed with diethyl ether, and dried under vacuum. Complexes with 4-Etpy, 2-Etpy, 2-Clpy, and CH_3CN were prepared in situ, immediately before the ESI-MS experiment, by dissolving $[Ru_3O(CH_3COO)_6(py)_2(CH_3OH)]PF_6$ in methanol and adding the desired L to this solution. Elemental analysis of $\mathbf{1}(PF_6)$ salts is provided as Supporting Information.

The mass spectrometric measurements were performed using a high-resolution hybrid quadrupole (Q) and orthogonal time-of-flight (Tof) mass spectrometer (QTof from Micromass, UK) operating in the positive ion mode. The temperature of the nebulizer was 200 °C, and the cone voltage was 40 V. The ESI-MS/MS experiments were performed via Q1 selection of the most abundant isotopologue ion of the complex, followed by collision-induced dissociation (CID) with argon at 10 eV energy in hexapole and Tof MS analysis of the ionic fragments.

Semiempirical molecular orbital calculations were carried out using the PM3(tm) method[13] within the HyperChem program from Hypercube.[14] This method has proven to give reasonable results for similar compounds,[15] and SCF molecular orbitals were obtained at the UHF level using 10^{-5} kcal mol^{-1} as the convergence limit. Geometry optimization was performed for all compounds and their fragments, using a conjugate gradient algorithm until reaching a rms of 10^{-4} kcal mol^{-1} Å^{-1}.

Results and Discussion

L Affinities. Figure 1a displays, as a representative example, the ESI-MS in the positive ion mode of a methanol solution of the $[Ru_3O(CH_3COO)_6(py)_2(pz)]PF_6$ complex. As expected, the intact singly charged cation is readily and gently transferred to the gas phase by ESI(+), the complex being unambiguously detected by MS as a characteristic multicomponent cluster of Ru_3-isotopologue ions (see inset). Using a tandem mass spectrometer with a hybrid QTof configuration, that is, with a quadrupole mass filter (Q), an rf-only hexapole collision cell (q), and a TOF mass analyzer, the most abundant isotopologue of $[Ru_3O(CH_3COO)_6(py)_2(pz)]^+$ of *m/z* 913 was selected (by Q) and dissociated via gentle 10 eV collisions with argon. As Scheme 2 (L = pz) depicts, two fragment ions were obtained as the main dissociation products (Figure 1b) owing to competitive loss of the terminal ligands. Clearly, the most abundant ion is that of *m/z* 833, indicating that pz is more easily released than py. The average values of the integrated peak areas are $A_L = 352$ and $A_{py} = 706$ in arbitrary units (Table 1), where A_L and A_{py} are the abundances of the fragment ions formed respectively when L (pz) and py are retained and consequently py and L are lost. The factor 1/2 was applied to A_L because loss of py is statistically favored due to the py:L stoichiometry of 2:1. Therefore, py binds more strongly than pz, as can be inferred from the ${}^1/_2A_L/A_{py} = 0.25$ value. These data will be correlated via Cooks' kinetic method[16] (see below).

Similar ESI-MS/MS experiments (Table 1) were performed for the complexes formed with a series of L. Since the binding strength of NO to the $[Ru_3O(CH_3COO)_6]^+$ core is much greater than that of py, that complex dissociates to form only the fragment ion $[Ru_3O(CH_3COO)_6(py)NO]^+$ of *m/z* 784. Accordingly for NO (a very strongly binding ligand), py is found to

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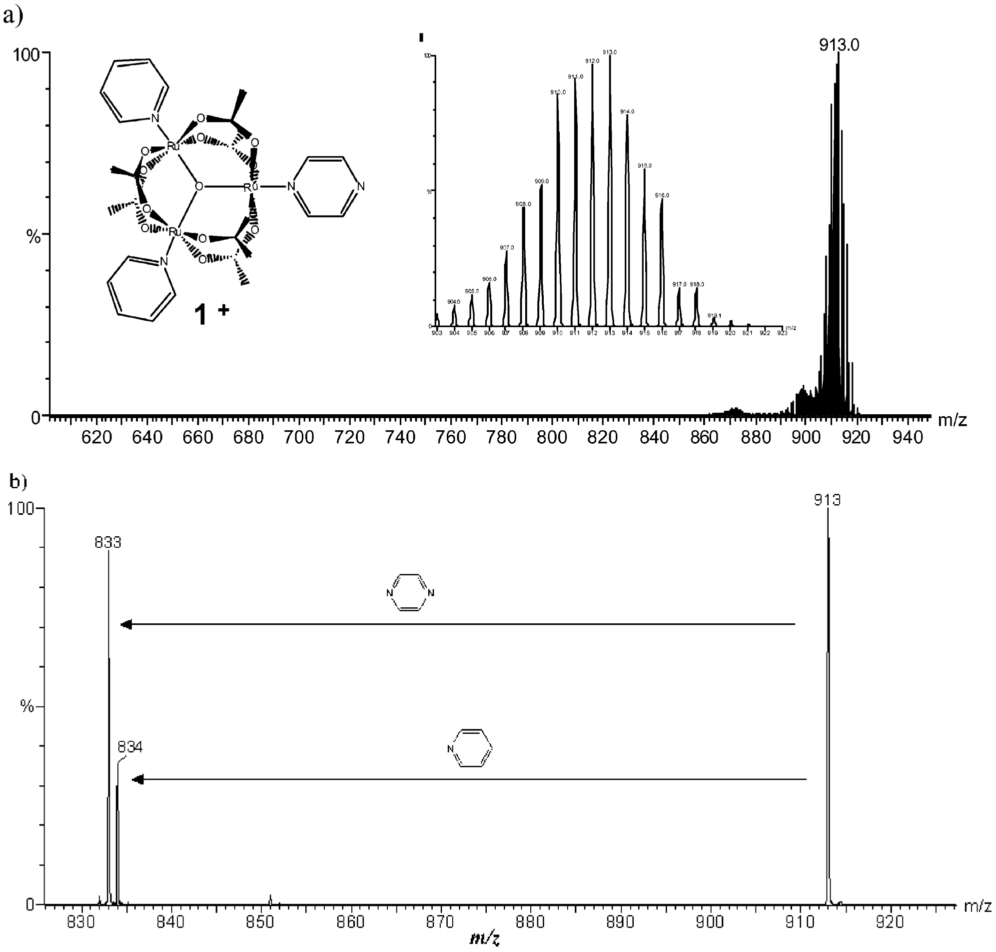
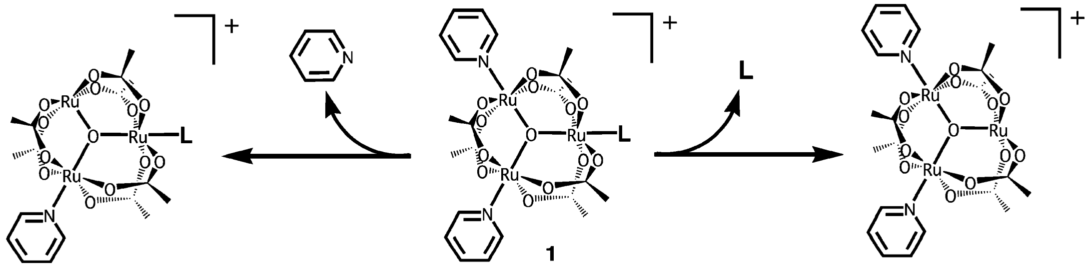
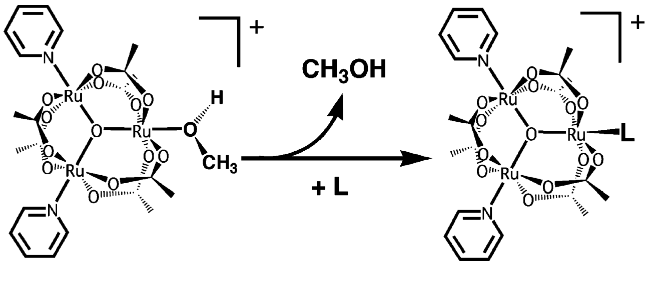


Figure 1. (a) ESI-MS of a methanolic solution of [Ru$_3$O(CH$_3$COO)$_6$(py)$_2$(pz)]PF$_6$. Note that [Ru$_3$O(CH$_3$COO)$_6$(py)$_2$(pz)]$^+$ is detected as a cluster of isotopologue ions (see inset) with a characteristic Ru$_3$ isotopic pattern. (b) ESI-MS/MS for 10 eV CID of the ion of *m*/*z* 913 (the most abundant isotopologue ion) leading to competitive dissociation of either py (*m*/*z* 834) or pz (*m*/*z* 833).

Scheme 2

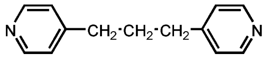
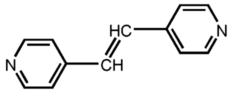
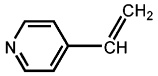
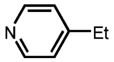
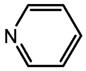
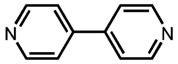
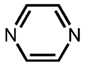
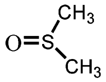
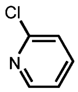
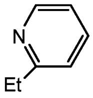


Scheme 3



be a too weakly binding reference ligand, and the $^1/_2A_L/A_{py}$ ratio (Table 1) could not be measured. Therefore to access the binding strength of NO, a reference ligand (L′) that binds to the [Ru$_3$O(CH$_3$COO)$_6$]$^+$ core much more strongly than py should be employed. Similarly, since the binding strength of py is much greater than those of methanol, acetonitrile, and water, CID of the respective complexes yields [Ru$_3$O(CH$_3$COO)$_6$(py)$_2$]$^+$ of *m*/*z* 833 (loss of L) as the single fragment ion. Therefore for these very weakly binding L, py is a too strongly binding reference ligand and again the respective $^1/_2A_L/A_{py}$ ratios (Table 1) could not be measured. The methanol, acetonitrile, and water complexes are, however, excellent starting materials for the synthesis of other mixed-ligand complexes suitable for ESI-MS/MS investigation. For example, the addition of a strongly binding L to the methanol solution of the [Ru$_3$O(CH$_3$COO)$_6$(py)$_2$(CH$_3$OH)]$^+$ complex promoted replacement of CH$_3$OH by L, thus generating the desired complex (Scheme 3). This procedure was therefore used to prepare and investigate via ESI-MS/MS the binding properties of the 4-Etpy, 2-Etpy, and 2-Clpy complexes. Simply, a few microliters of these ligands was added to a methanol solution of the [Ru$_3$O(CH$_3$COO)$_6$(py)$_2$(CH$_3$OH)]PF$_6$ complex and, after few minutes, the resulting mixture was electrosprayed. Both the parent and product complexes were

Table 1. Absolute (A_L and A_{py} in arbitrary units) and Relative Abundances[a] ($^1/_2A_L/A_{py}$) of the Two Fragment Ions Formed after Selection and Gentle Low-Energy (5−10 eV) Collision-Induced Dissociation of the Most Abundant Isotopologue of $[Ru_3O(CH_3COO)_6(py)_2(L)]^+$ (1^+) Complexes, and the Affinity of L for $[Ru_3O(CH_3COO)_6]^+$ as Estimated by PM3(tm) Calculations

L ligand	A_L	A_{Py}	$\frac{1}{2}A_L/A_{py}$	PM3(tm) L affinity (kcal mol^{-1})
NO	238	0	—	52.9
	113	16	3.53	—
	44	11	2.00	—
	374	105	1.78	20.3
	47	16	1.47	19.5
	-	-	1.00	19.6
	128	86	0.74	18.9
	352	706	0.25	17.4
	44	577	0.040	—
	4	50	0.040	11.1
	8	260	0.030	9.7
CH_3OH	0	443	—	—
CH_3CN	0	345	—	—
H_2O	0	23	—	—

[a] The intensity of the fragment ion relative to the loss of pyridine (A_L) has been divided by 2 to account for the statistical factor; see text.

detected, and the desired product complex was selected and subjected to CID.

The $^1/_2A_L/A_{py}$ ratios (Table 1) determined from the ESI-MS/MS data were used to order the complexes according to the intrinsic L affinities to $[Ru_3O(CH_3COO)_6]^+$, that is, NO > BPP > BPE > vpy > 4-Etpy > py > 4,4′-bpy > pz > DMSO ~ 2-Clpy > 2-Etpy > CH_3OH ~ CH_3CN ~ H_2O. This intrinsic order measured in the gas phase can now be compared with the behavior of those complexes in solution. For example, the coordinating solvents DMSO, CH_3OH, CH_3CN, and H_2O are herein shown to be, intrinsically, the weakest ligands to the $[Ru_3O(CH_3COO)_6]^+$ core. This result is in agreement with the behavior of the corresponding solvated complexes, and the lability of such L ligands in solution is explored to obtain precursors for preparation purposes, as already discussed.

DMSO is an interesting ligand because, depending on the electronic properties of the metal ion, it binds through either the O or the S atom. To $[Ru_3O(CH_3COO)_6]^+$, DMSO binds through the O atom, as expected for a metal center with preponderant hard character (the ruthenium ions are all in the

+3 oxidation state). This binding is confirmed by the low binding affinity of pz, a quite strong π-acid and weak σ-donor ligand. Nevertheless, the DMSO complex is the only one with a conventional solvent as the L ligand that provided the $[Ru_3O(CH_3COO)_6(py)(L)]^+$ fragment cation in significant amount upon CID.

Although the ruthenium ions in $[Ru_3O(CH_3COO)_6]^+$ are normally considered to be Ru(III), the electronic coupling between them and the central oxygen atom is strong enough to induce spin-pairing, leaving one electron completely delocalized in the triangular center. The chemistry of $[Ru_3O(CH_3COO)_6]^+$ is therefore intermediate between that of the Ru(III) and Ru(II) species. Typically, Ru(II) chemistry is dominated by $d\pi \rightarrow p\pi$ back-bonding interactions, which stabilize preferentially the complexes with π-acceptor ligands, such as pz and κS-DMSO. In contrast, Ru(III) complexes are preferentially stabilized by σ,π-donor ligands, binding DMSO via the oxygen. This dual character may explain why the DMSO binding is stronger than with a typical σ-donor such as H_2O and a π-acceptor such as CH_3CN.

When we examine the other binding properties complied in Table 1, the π-donor and π-acceptor properties of L seem to match the dual behavior of $[Ru_3O(CH_3COO)_6]^+$, leading to the observed dissociation trends. For instance, NO is by far the most strongly bound ligand. $[Ru_3O(CH_3COO)_6(py)_2(NO)]PF_6$ has actually been described in terms of the delocalized electronic configuration $Ru^{III}\,Ru^{III}\,Ru^{III}O - NO^0 \leftrightarrow Ru^{III}\,Ru^{III}\,Ru^{II}O - NO^+$. The strong involvement of NO π*-orbitals in the back-bonding interaction with $[Ru_3O(CH_3COO)_6]^+$ accounts for the fact that the $NO{-}[Ru_3O(CH_3COO)_6]^+$ bond is much stronger than $py{-}[Ru_3O(CH_3COO)_6]^+$.[11] Actually, $NO{-}[Ru_3O(CH_3COO)_6]^+$ complexes are better described as a diamagnetic species in which the unpaired electron of the $[Ru_3O(CH_3COO)_6]^+$ core and the NO ligand are paired in a molecular orbital localized in the triruthenium cluster. The representative complexes where L is a pyridinic ligand appear as a distinct series, except for pz, which dissociates more easily than py. It is well known that the π-acidic pyrazine ligand stabilizes better the reduced triruthenium complex, i.e., $[Ru_3O(CH_3COO)_6(py)_2(pz)]^0$, rather than the oxidized form studied here. Therefore, in this series of complexes, the σ,π-donor properties of L should be more important than their π-acceptor properties.

Steric Effects on L Affinity. The selection and dissociation of the pair of isomeric complexes with 4-Etpy and 2-Etpy offer us the unique opportunity to evaluate the extent of steric effects on L binding affinities to $[Ru_3O(CH_3COO)_6]^+$. As expected from the electron-donating ability of the ethyl group, 4-Etpy shows *greater* binding affinity than py with a $^1/_2A_L/A_{py}$ ratio of 1.47 (Table 1). However, the steric effects of the 2-ethyl substituent are as pronounced as to enlarge the Ru−L bond length to such an extent that 2-Etpy is one of the weakest ligands ($^1/_2A_L/A_{py}$ ratio of 0.030, Table 1). For 2-Clpy, probably a combination of steric effects and electron-withdrawing nature contributes to reduce its binding affinity, giving a $^1/_2A_LA_{py}$ ratio as low as 0.040 (Table 1).

Cooks' Kinetic Method. Cooks and co-workers[16] have developed a MS method (CKM) for measuring bond strengths as well as a diverse set of properties of gaseous ions and molecules including steric, isotopic, agostic, and stereoelectronic effects.[17] CKM employs typically gaseous and mixed ionic complexes of the $M1{-}{-}X^+{-}{-}M2$ type where M is a neutral molecule or radical and X^+ is a proton or other ionic species. Gentle dissociation of such gaseous weakly bound complexes yields two fragment ions, M_1X^+ and M_2X^+, due to competing losses of M_1 or M_2. The weaker bonds are more easily broken; hence, the more strongly bonded species, either M_1X^+ or M_2X^+, is observed as the more abundant (or exclusive) fragment ion. In its simplest (and nearly as reliable) form,[16] CKM considers that the $[M_1X^+]$ and $[M_2X^+]$ abundances (A_L and A_{py} for $\mathbf{1}^+$) correlate directly to the difference in $M_1{-}{-}{-}X^+$ and $M_2{-}{-}{-}X^+$ bond strengths, hence to the affinities of M_1 and M_2 to X^+. For $\mathbf{1}^+$, this correlation is given by eq 1, in which T_{eff} is the effective temperature of the complex.

$$\ln(^1/_2A_L/A_{py}) = \Delta([Ru_3O(CH_3COO)_6]^+ \text{ affinity})/RT_{eff} \quad (1)$$

A systematic study[18] has demonstrated that CKM is applicable to measure substituted pyridine binding affinities to relatively simple organic and inorganic cations and metal cations and complexes, e.g., for $X^+ = Cl^+$, $OCNCO^+$, SF_3^+, SiF_n^+, Fe^+, Co^+, Ni^+, $CpFe^+$, $CpCo^+$, and $CpNi^+$. By comparing the dissociation of analogous X^+- and H^+-bound dimers composed of a hindered and an unhindered pyridine, eletronic effects have been canceled out and steric effects of *ortho*-pyridine substituents ordered and measured. The intramolecular steric effects of *ortho* substituents (measured as S^k values) were found to increase not only with size but also as the affinity of the *ortho*-substituted pyridine to X^+ increases, due to shortening of the pyridine−cation bond. These intrinsic S^k values were found to fall in the same order as that for corresponding steric parameters obtained by solution kinetic measurements.[18a] CKM has also been applied to measure affinities of other ligands to various simple metal cations[19] such as Ag^+, Ni^+, Co^+, $CoCl^+$, Fe^+, Na^+, Cs^+, Rb^+, Li^+ and Ca^{2+}.

The access to a set of gaseous $\mathbf{1}^+$ and their dissociation patterns allows us to investigate whether CKM could be extended to much larger and more structurally intricate polymetallic complexes. Unfortunately, no experimental values of L affinities to $[Ru_3O(CH_3COO)_6]^+$ are available for comparison. However, the rapid development of computational chemistry is making it feasible to deal with quite complex molecular systems and estimate their properties with good accuracy.

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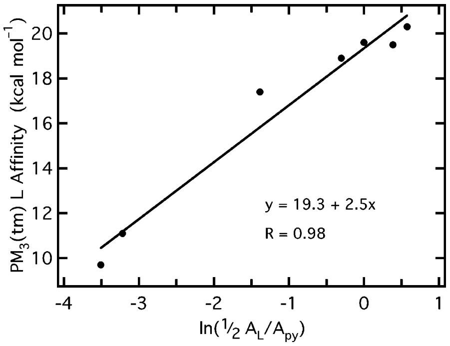

Figure 2. CKM plot for PM3(tm) L affinities versus ln $^1/_2A_L/A_{py}$ (Table 1).

Accordingly, we employed theoretical calculations to estimated the affinities of the various L to $[Ru_3O(CH_3COO)_6]^+$, hence to verify whether they correlate via eq 1 with the experimental $^1/_2A_{py}/A_L$ ratios. To calculate L affinities according to eqs 2 and 3, PM3(tm) geometry optimization was attempted for the 14 **1**$^+$ complexes (Table 1) as well as for all ligands (L) and the $[Ru_3O(OAc)_6(py)_2]^+$ fragment:

$$[Ru_3O(OAc)_6(py)_2L]^+ \rightarrow [Ru_3O(OAc)_6(py)_2]^+ + L \quad (2)$$

$$\text{L affinity} = E([Ru_3O(OAc)_6(py)_2L]^+) - (E([Ru_3O(OAc)_6(py)_2]^+) + E(L)) \quad (3)$$

However, geometries of the DMSO, CH_3OH, CH_3CN, and H_2O complexes failed to converge properly, perhaps because of their more weakly bonded nature, as can be inferred from the experimental results (Table 1). The calculations were also problematic for the BPP and BPE complexes with such relatively large ligands, since they lead to unreasonable optimized geometries and L affinities. However, the optimized geometries obtained for the other eight complexes here investigated were in good agreement with available crystallographic data.[1]

The PM3(tm)-calculated L affinities (Table 1) for seven of such complexes were then plotted against ln $^1/_2A_L/A_{py}$ (Figure 2). The good linear correlation ($R = 0.98$) indicates that CKM is indeed reliable to order and measure relative L affinities via eq 1. From the slope of the CKM plot (Figure 2) a T_{eff} of 1258 K ($R = 1.987 \times 10^{-3}$ kcal mol^{-1} K^{-1}) is calculated for the gaseous **1**$^+$ as formed, sampled, and dissociated by the current ESI-MS/MS conditions. This T_{eff} is relatively high,[20] especially when compared to T_{eff} around 400−800 K normally obtained for simple metal cation clusters,[19] and indicates that ligands in **1**$^+$ are intrinsically quite strongly bonded.

Conclusion

A series of $[Ru_3O(CH_3COO)_6(py)_2(L)]^+$ complexes (**1**$^+$) with various ligands L and py as a reference ligand have been synthesized and gently transferred for ESI-MS characterization directly from methanol solutions to the gas-phase environment of a mass spectrometer. Gentle dissociation of several gaseous **1**$^+$ via ESI-MS/MS experiments was found to afford two fragment ions due to the loss of either L or py. The experimental relative L affinity to $[Ru_3O(CH_3COO)_6]^+$ as determined using Cooks' kinetic method was found to correlate linearly ($R = 0.98$) with theoretical PM3(tm) L affinities. Steric effects in *ortho*-substituted pyridines were found to greatly reduce the affinities (binding strengths) of these crowed ligands. A T_{eff} of 1258 K was found for **1**$^+$, which is considerably higher than average T_{eff} measured for simple metal complexes. This relatively high T_{eff} indicates that gaseous **1**$^+$ are strongly bound complexes. As we demonstrated here for **1**$^+$, CKM seems also to be applicable to order and measure L affinities for large and structurally intricate polymetallic complexes.

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Supporting Information Available: Elemental analyses of complexes **1**(L)PF_6. This material is available free of charge via the Internet at http://pubs.acs.org.

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