We report here a systematic photoelectron spectroscopy (PES) and theoretical study of divalent transition metal (TM) EDTA complexes \([\text{EDTA} \cdot \text{M(II)}]^2^-\) (TM = V–Zn), along with the Ca(II) species for comparison. Gaseous TM dianions (TM = Ca, Mn, Co, Ni, Cu and Zn) were successfully generated via electrospray ionization, and their PE spectra, with 157, 193, and 266 nm photons, were obtained at 20 K. The spectrum of each TM complex shows an extra peak at the lowest electron binding energy (eBE), compared to that of \([\text{EDTA} \cdot \text{Ca(II)}]^2^-\). DFT calculations indicate a hexacoordinated metal–EDTA binding motif for all complexes, from which the vertical detachment energies (VDEs) are calculated and these agree well with the experimental values. The calculations further predict negative or very small VDEs for TM(II) = V, Cr, and Fe, providing a rational explanation for why these three dianionic species are not observed in the gas phase. Direct spectral comparison, electron spin density differences, and MO analyses indicate that the least bound electrons are derived from TM d electrons with appreciable ligand

Qinqin Yuan,‡§ Xiang-Tao Kong,‡ Gao-Lei Hou, a Ling Jiang †b and Xue-Bin Wang †a

Received 12th November 2018, Accepted 21st November 2018
DOI: 10.1039/c8fd00175h
contributions, in contrast to [EDTA-Ca(II)]^{2-}, in which the detachment is entirely derived from the ligand. The extent of ligand modulation, i.e. non-innocence of EDTA ligands in the oxidation process, is found to vary across the 3rd row of TMs. Comparing the gas-phase VDEs of [EDTA-TM(II)]^{2-} with the 3rd ionization potentials of TMs and solution phase oxidation potentials reveals intrinsic correlations among these three quantities, with deviations being largely modulated by the ligand participation. The detailed microscopic information about the intrinsic electronic structures and bonding motifs of these complexes obtained in this work will help better understand the rich redox chemistries of these ubiquitous species under diverse environments. The present work, along with our previous studies, indicates that PES coupled with electrospray ionization is a unique ion spectroscopic tool that not only provides intrinsic electronic structure and bonding information about redox species, but also can predict the related electron transfer chemistries with quantitative capability.

Introduction

Metal organic complexes have been extensively investigated as models of metalloenzyme active sizes, as enzyme inhibitors, and as DNA cleavage agents.\textsuperscript{1–5} It has been found that chelating ligands can significantly modulate the redox behavior of metal ions and influence DNA nuclease activities. As one of the most common organic ligands, ethylenediaminetetraacetate (EDTA\textsuperscript{4-}), the conjugate base of an aminopolycarboxylic acid, has “bifunctional chelating groups” of carboxylate and amine groups, and can chelate with almost every metal cation in the periodic table using its two nitrogen and four oxygen atoms to form thermodynamically favorable [EDTA•M] complexes. Diverse metal-specific biological and medical functions of divalent metal chelate complexes have been recognized,\textsuperscript{6–10} and the related redox potentials under physiologically relevant conditions have been estimated.\textsuperscript{5}

A variety of analytical methods have been employed to characterize metal EDTA complexes in solutions\textsuperscript{11–17} and crystals.\textsuperscript{18–23} Due to the complications associated with bulk environments, and, in particular, the influences of pH value in solutions, unambiguous coordination motifs between EDTA and various metals are still lacking, and remain considerably uncertain.\textsuperscript{13,15,16} Gas-phase ion spectroscopy coupled with electrospray ionization and combined with quantum chemical calculations has been demonstrated to be a powerful technique to obtain intrinsic geometries and electronic structures of exotic species, intermediates, and microsolvated clusters from solutions without bulk perturbations.\textsuperscript{24–33} Because photodetachment is a process involving the ejection of an electron from anionic species, analogous to a half electron transfer reaction (due to no electron acceptor),\textsuperscript{34} explicit electronic structure information mimicking the oxidation process of redox species is encoded in the resulting photoelectron (PE) spectrum, in which the electron binding energy (eBE) derived from the 1\textsuperscript{st} spectral band with the lowest eBE correlates to the intrinsic oxidation potential. Our recent study on a series of EDTA trivalent metal complexes, [EDTA•M(III)]\textsuperscript{-}, revealed distinctly different PE spectral patterns for transition metal complexes with d electrons (M = V–Co) compared to those without d electrons (M = Al, Sc), providing a molecular-level rationale to understand the special redox behavior of vanadium species in biological cells.\textsuperscript{35} Given the fact that EDTA divalent metal complexes,
[EDTA·M(II)]^{2−}, are ubiquitous and exhibit rich redox chemistries under diverse environments,5–10 herein, we conducted a systematic investigation by employing electrospray ionization photoelectron spectroscopy (PES) and theoretical modeling on a series of such complexes across the 3rd row metals (M = Ca, V–Zn) to probe the EDTA–M binding motifs, to determine their geometries and intrinsic electronic structures, and to examine the metal-specific eBE variation and how well the eBE trend is correlated with the redox potentials measured in solutions.

Experimental methodology

The experiments were carried out using a PNNL size-selective, cryogenic, electrospray ionization PES instrument.28 [EDTA·Ca(II)]^{2−} and [EDTA·Cu(II)]^{2−} dianions were produced directly via spraying into vacuum 1.0 mM solutions of EDTA calcium disodium salt and EDTA copper(II) disodium salt dissolved in a mixture of H₂O/CH₃CN (1 : 3) solvents, respectively. [EDTA·Mn(II)]^{2−} was generated through spraying a 1.0 mM aqueous acetonitrile solution of manganese(III) acetate dihydrate and disodium EDTA salts, where a disproportionation reaction occurred. In order to produce all other dianionic complexes, [EDTA·M(II)]^{2−}, 1.0 mM aqueous acetonitrile solutions of mixed MCl₂ and EDTA disodium salts were prepared and sprayed.

The generated dianionic complexes were guided by two RF only quadrupoles and a 90° bender into a cryogenic 3D ion trap, where they were accumulated and collisionally cooled with buffer gas (20% H₂ balanced in helium) for 20–100 ms. In these experiments, the ion trap was operated at 20 K to minimize the appearance of extra spectral features due to hot bands and improve energy resolution. The cryogenic anions were then pulsed out into the extraction zone of a time-of-flight (TOF) mass spectrometer at a 10 Hz repetition rate, and the desired dianions were each mass-selected and decelerated before being photodetached in the interaction zone with a laser beam. Three different laser wavelengths, 266 nm (4.661 eV from an Nd:YAG laser), 193 nm (6.424 eV from an ArF laser), and 157 nm (7.867 eV from an F₂ laser), were used for photodetachment. All lasers were operated at a 20 Hz repetition rate with the ion beam off at alternating laser shots, affording shot-by-shot background subtraction. Photoelectrons were collected at ~100% efficiency with a magnetic bottle and analyzed in a 5.2 m long electron flight tube. The resultant TOF photoelectron spectrum was converted into an electron kinetic energy (eKE) spectrum, calibrated using the known spectra of I⁻ (ref. 36), OsCl₂⁻ (ref. 37) and Au(CN)₂⁻ (ref. 38). The electron binding energy spectra, presented in the manuscript, were obtained by subtracting the kinetic energy spectra from the detachment photon energies. The electron energy resolution was about 2% (i.e. ~20 meV for 1 eV kinetic energy electrons).

Theoretical methodology

Density functional theory (DFT) calculations, using PBE0, B3LYP, MN12SX, BP86, and MN15 functionals with the 6-311+G(d,p) basis set for all atoms, were carried out for [EDTA·M(III)]^{2−} (M = Ca, V–Zn). Structures were optimized using tight convergence criteria without any symmetry restrictions. Harmonic vibrational frequency analyses were performed to confirm that all structures were real minima. All relative energies reported include zero-point energy corrections.
Theoretical vertical detachment energies (VDEs) were calculated as the electronic energy differences between the singly charged anions and the corresponding dianions both at the optimized dianions’ geometries. Table S1 in the ESI† compares the experimental VDEs with the theoretical VDEs, calculated using these five different functionals for \([\text{EDTA} \cdot \text{M(II)}]^2^-\) (M = Ca, Mn, Co, Ni, Cu and Zn). It can be seen that the MN12SX functional yields the best VDEs in comparison to the experimental values for the complexes containing 3d electrons, compared to the other functionals, while M06-2X is a good choice to calculate the VDEs for those without 3d electrons, i.e. the Ca(II) complex. A similar preference for different functionals was found in our recent study for trivalent metal EDTA systems.\textsuperscript{35} In this work, for the convenience of discussion, we present the MN12SX results for all \([\text{EDTA} \cdot \text{M(II)}]^2^-\) (M = Ca, V–Zn) complexes in the main text unless otherwise noted. Different spin states were also considered for the complexes with unpaired 3d electrons, M = Mn, Co and Ni, as shown in Table S2;\textsuperscript{†} this suggested that high spin states are more stable than low spin states by at least 1.0 eV in energy. The excited state energies of the singly charged anions, accessible via photodetaching the corresponding dianions, were determined using time-dependent DFT (TD-DFT) calculations at the dianions’ geometries. All quantum chemical calculations were performed using the Gaussian 09 program suite.\textsuperscript{39}

Experimental results

We have made intentional efforts to conduct a holistic study on \([\text{EDTA} \cdot \text{M(II)}]^2^-\) complexes across the third-row transition metals (M = V–Zn). \([\text{EDTA} \cdot \text{M(II)}]^2^-\) type dianions were generated abundantly via electrospray ionization for M = Mn, Co, Ni, Cu, and Zn, but not for M = V, Cr and Fe. For the latter three metals, \([\text{EDTA} \cdot \text{M(III)}]^-\) were observed instead, presumably due to the fact that the corresponding M(II) dianions were very sensitive to oxidation, and were easily oxidized to the M(III) singly charged complexes by adventitious O\textsubscript{2} during electrospraying. The PE spectra of \([\text{EDTA} \cdot \text{M(II)}]^-\) (V, Cr, Fe) were reported in our previous publication.\textsuperscript{35} This ‘negative’ portion of the experiments does, however, suggest that \([\text{EDTA} \cdot \text{V(II)}/\text{Cr(II)/Fe(II)}]^2^-\) should have very small if not negative VDE values, which is confirmed by our theoretical calculations as shown in the next sections.

Photodetachment photoelectron spectroscopic measurements of \([\text{EDTA} \cdot \text{M(II)}]^2^-\) (M = Ca, Mn, Co, Ni, Cu, and Zn) were carried out at 20 K using 157, 193, and 266 nm photons, and the results are shown in Fig. 1. The 157 nm PE spectrum of \([\text{EDTA} \cdot \text{Ca(II)}]^2^-\) shows a broad band in the eBE range of 2.4 to 4.6 eV consisting of two discernible features, A & B, while those of the transition metal (TM = Mn, Co, Ni, Cu, and Zn) complexes each possess the main spectral bands A & B, similar to that in the Ca case. In addition, a weak band X at a low eBE is seen in each of the Mn, Co, Ni, Cu, and Zn complex spectra, whose binding energy increases with TM atomic number. The PE spectrum of each complex at 193 nm looks similar to that at 157 nm, with the intensity of feature A slightly increased, while at 266 nm, only feature A is observed for M = Ca, features X & A are observed for M = Mn, Co, Ni and Zn, and features X & B are observed for M = Cu (Fig. 1).

A repulsive Coulomb barrier (RCB), a general feature in photodetachment of multiply charged anions (MCAs), leads to a hallmark in any PE spectrum of a MCA, resulting in truncation of any PE signals with eKE of electrons less than the height of the RCB and significantly reducing electron signals for electrons.
with eKE \approx \text{RCB} \ (\text{Fig. S1}^{\dagger}).^{40,41} \text{ The cutoffs and intensity variation of the spectral features observed at different wavelengths for each species in Fig. 1 are direct results of the dianionic nature of each complex. On the one hand, at 193 nm, the majority of feature B is seen for each species, indicating that the RCB should be less than 2.4 eV (by subtracting 4.0 eV from 6.4 eV). On the other hand, at 266 nm, feature A is seen either red-shifted or with its intensity appreciably reduced, suggesting the RCB should be larger than 1.6 eV (by subtracting 3.0 eV from 4.6 eV). A more close examination of the spectral cutoff positions at 193 and 266 nm leads to an approximated 2.0 eV RCB for these complexes (Table 1). It is worth pointing out that feature B for each complex should not be seen at 266 nm because of the RCB cutoff effect. However, a strong peak at the B position in the Cu(II) spectrum is present at 266 nm (Fig. 1), which is most likely due to resonant autodetachment.}^{42}

![Fig. 1 20 K photoelectron spectra of [EDTA-M(II)]^{2-} (M = Ca, Mn, Co, Ni, Cu, and Zn) at 157 nm (7.867 eV, red), 193 nm (6.424 eV, blue), and 266 nm (4.661 eV, green).](image)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Expt. VDE (eV)</td>
<td>2.70(10)</td>
<td>1.15(10)</td>
<td>1.70(10)</td>
<td>1.73(10)</td>
<td>1.78(10)</td>
<td>2.20(20)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calc. VDE (eV)</td>
<td>2.33(2.90)</td>
<td>(-0.42)</td>
<td>0.16</td>
<td>1.16</td>
<td>0.64</td>
<td>1.63</td>
<td>1.66</td>
<td>2.08</td>
<td></td>
</tr>
<tr>
<td>Expt. RCB (eV)</td>
<td>(~2.0)</td>
<td>(~2.0)</td>
<td>(~1.9)</td>
<td>(~2.0)</td>
<td>(~2.0)</td>
<td>(~2.0)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(a\) Numbers in parentheses represent the experimental uncertainties in the last digits. 
\(b\) MN12SX/6-31+G(d,p) VDEs, unless otherwise noted. 
\(c\) The calculated VDE for Ca(II) in parentheses is the M06-2X/6-311+G(d,p) value.
The first spectral band for [EDTA·Ca(II)]$_2^{2-}$ is feature A, in which the metal Ca(II) has no 3d electrons, while that for each [EDTA·TM(II)]$_2^{2-}$ species containing 3d electrons is feature X. Similar observations were reported in the PES study of [EDTA·M(III)]$^-$. The experimental VDE for [EDTA·M(II)]$_2^{2-}$ was measured from the maximum of the first peak in each spectrum, and is 2.70 ± 0.10 (Ca), 1.15 ± 0.10 (Mn), 1.70 ± 0.10 (Co), 1.73 ± 0.10 (Ni), 1.78 ± 0.10 (Cu), and 2.20 ± 0.20 eV (Zn) (Table 1), respectively.

Theoretical results and discussion

A. Optimized structures of [EDTA·M(II)]$_2^{2-}$

Three metal ligand binding motifs, including hexadentate (Iso A), pentadentate (Iso B) and tetradentate (Iso C) EDTA metal complexes, were optimized and are presented in Fig. 2. Our calculations show that the quasi-octahedral type structure with the hexadentate ligand (Iso A) is the most stable isomer for all metal complexes (Table S3, ESI†). Penta-coordinated Iso B is calculated to be the next lowest energy isomer, being 0.75 (Ca), 0.73 (V), 0.44 (Cr), 0.42 (Mn), 0.25 (Fe), 0.15 (Co), 0.34 (Ni), 0.06 (Cu) and 0.23 eV (Zn) higher in energy than Iso A. The binding motif of tetra-coordinated Iso C is found to be much less favorable, by 0.8 eV compared to Iso A for all species except for Cu, which is 0.21 eV higher in energy (Table S4†).

Since isomers A and B are close in energy, it is useful to calculate the transition barriers between these two isomers, to help estimate the existence of one or both isomers in the experiments. Our DFT calculations show that there exist substantial barriers between Iso A and Iso B for the Ca, Mn, Co, Ni, and Zn complexes, i.e. 1.34 (Ca), 1.09 (Mn), 0.86 (Co), 1.05 (Ni), and 0.91 eV (Zn), while there exists an appreciably smaller barrier of 0.29 eV for the Cu(II) species (Table S4†). The above energetic and barrier analyses suggest the dominance of the hexadentate Iso A for [EDTA·M(II)]$_2^{2-}$ (M = Ca, Mn, Co, Ni and Zn) in the experiments. The coexistence of the nearly isoenergetic isomers A and B is likely for [EDTA·Cu(II)]$_2^{2-}$, because its calculated spectrum also matches a part of the observed spectrum (vide infra).

B. Calculated VDEs and simulated spectra

Table 1 lists the MN12SX/6-311+G(d,p) VDEs of all [EDTA·M(II)]$_2^{2-}$ complexes, as well as the M06-2X/6-311+G(d,p) VDE for the Ca species, based on the most stable

---

[Fig. 2 Three binding motifs for [EDTA·M(II)]$_2^{2-}$ complexes with hexa-, penta- and tetra-coordination (H, light grey; C, grey; O, red; N, blue; M, light brown).]
quasi-octahedral isomer A. Comparing with the experimental value for the Ca complex, the M06-2X functional overestimates the VDE by 0.2 eV, while MN12SX underestimates the VDE by 0.37 eV. For all TM complexes, the agreement between the experimental and MN12SX VDEs is excellent, i.e. 1.15/1.16 (Mn), 1.70/1.64 (Co), 1.73/1.63 (Ni), 1.78/1.66 (Cu) and 2.20/2.08 eV (Zn). Consequently, the MN12SX/6-311+G(d,p) methodology was also utilized to predict the VDE values for the three [EDTA·M(u)]2− (M = V, Cr, Fe) complexes that could not be generated in our experiments. As shown in Table 1, the calculated VDEs, −0.42, 0.16, and 0.64 eV for V, Cr and Fe, respectively, are either negative or very small, suggesting that these dianionic complexes are readily oxidized, which is consistent with the absence of these three complexes in the present experiments.

Fig. 3 shows a comparison of the TD-DFT simulated spectra of the lowest isomers for M(u) = Ca, Mn, Co, Ni, Cu, and Zn to the experimental spectra. The extra spectral peaks near the photon energy limit (green) in the simulated spectra are not expected to be observed in the experimental spectra, due to the RCB cutoff for photodetaching MCAs. It can be seen from Fig. 3 that the predicted band positions and overall patterns calculated from the lowest energy Iso A for each species match the experimental spectra reasonably well, except for [EDTA·Ca(u)]2−, for which the simulated spectrum is seen to shift to low eBE values. This is because, as discussed above, the MN12SX functional underestimates the VDE of the Ca species. The good agreement between the simulated and experimental spectra strongly suggests that isomer A, the quasi-octahedral structure with a hexadentate EDTA, largely contributes to the experimental spectrum for each complex. In the case of [EDTA·Cu]2−, it is likely that the nearly degenerate Iso B with a pentadentate EDTA coexists and contributes to the experimental spectrum as well.

C. Anti-correlation between electron detachment energy and the d component in HOMOs

The PE spectra in Fig. 1 provide explicit electronic structure information about [EDTA·M]2− complexes. Peak X at low eBE values is seen in the spectrum of each M = Mn, Co, Ni, Cu and Zn complex that formally contains 3d electrons, while it is missing for M = Ca in which no d electrons are present. Similar observations were reported recently in the PES study on [EDTA·M(m)]− (M = Al, Sc, and V–Co).35 The VDE of the TM–EDTA complex, measured from the X band, increases in the order of Mn < Co < Ni < Cu < Zn, with the highest VDE of the Ca–EDTA complex being measured from the A band. To obtain a qualitative picture on where the least bound electrons are being detached, electron spin density differences between [EDTA·M]− anions and [EDTA·M]2− dianions at the optimized dianionic geometries were computed based on Mulliken population analyses (Fig. 4). A salient feature is that the electron is entirely detached from the O atoms of the EDTA ligand for [EDTA·Ca]2−, whereas, for TM = V–Zn i.e. with d electrons, detachment is derived significantly from the V(n)–Cu(n) metal cores, and noticeably from Zn(n), which has a d10 configuration. Molecular orbital (MO) analyses of the highest occupied (HO) MOs (Fig. S2†) should further lead to insightful information about the nature of the detachment process to remove the least bound electrons. As listed in Table 2 and plotted in Fig. 5, there exists a remarkable anti-correlation between the metal contribution in the HOMOs and
Fig. 3 MN12SX simulated PE spectra (black and green) and stick spectra (blue) of the lowest isomers for [EDTA·M(II)]$_2^-$ complexes, in comparison to the corresponding experimental spectra at 157 nm (red). Panels (a), (b), (c), (d), and (f) compare the simulated spectra from Iso A of the Ca, Mn, Co, Ni, and Zn complexes with their corresponding experimental spectra, and panel (e) compares the simulated spectra from Iso A and Iso B of the Cu(II) complex with the experimental one. The simulated stick spectrum for each complex was generated using the calculated VDE and TD-DFT excitation energies, and the simulated spectrum was obtained by convoluting the stick spectrum with Gaussian functions of 0.1 eV full width at half maximum for each stick. The predicted spectral bands at high eBE values (green) will not be observed in experimental spectra due to the spectral cutoff through repulsive Coulomb barriers.
the VDEs across the entire \([\text{EDTA-M}^{(II)}]^2^-\) series. A similar anti-correlation between the metal % in the HOMOs and VDEs was also observed in photo-detachment of \([\text{EDTA-M}^{(III)}]^-\) as well.

**Table 2** Molecular orbital analyses of \([\text{EDTA-M}^{(ii)}]^2^-\) \((\text{M} = \text{Ca, V–Zn})\) HOMOs, and the correlation between metal components in the HOMOs and experimental/calculated VDEs

<table>
<thead>
<tr>
<th>([\text{EDTA-M}^{(ii)}]^2^-)</th>
<th>Ca(II)</th>
<th>V(II)</th>
<th>Cr(II)</th>
<th>Mn(II)</th>
<th>Fe(II)</th>
<th>Co(II)</th>
<th>Ni(II)</th>
<th>Cu(II)</th>
<th>Zn(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expt. (VDE) (eV)</td>
<td>2.70</td>
<td>1.15</td>
<td>1.16</td>
<td>1.70</td>
<td>1.73</td>
<td>1.78</td>
<td>2.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Theo. VDE (eV)</td>
<td>2.33</td>
<td>0.42</td>
<td>0.16</td>
<td>1.16</td>
<td>0.64</td>
<td>1.64</td>
<td>1.63</td>
<td>1.66</td>
<td>2.08</td>
</tr>
<tr>
<td>Metal atoms (%)</td>
<td>80.80</td>
<td>85.60</td>
<td>69.70</td>
<td>50.70</td>
<td>84.10</td>
<td>22.90</td>
<td>22.20</td>
<td>12.70</td>
<td>2.70</td>
</tr>
<tr>
<td>N atoms (%)</td>
<td>27.30</td>
<td>0.20</td>
<td>15.80</td>
<td>3.80</td>
<td>0.50</td>
<td>31.90</td>
<td>28.80</td>
<td>37.90</td>
<td>29.00</td>
</tr>
<tr>
<td>O atoms (%)</td>
<td>45.30</td>
<td>9.50</td>
<td>8.70</td>
<td>42.10</td>
<td>13.90</td>
<td>32.40</td>
<td>37.90</td>
<td>30.20</td>
<td>47.60</td>
</tr>
<tr>
<td>C atoms (%)</td>
<td>20.20</td>
<td>3.90</td>
<td>2.50</td>
<td>2.50</td>
<td>2.00</td>
<td>7.10</td>
<td>6.20</td>
<td>11.00</td>
<td>14.40</td>
</tr>
</tbody>
</table>

**D. Interconnections between the gas phase VDEs, solution phase redox potentials, and third ionization potentials of metals**

The half-reaction \([\text{EDTA-M}^{(ii)}]^2^-\) \((\text{aq}) \rightarrow [\text{EDTA-M}^{(iii)}]^-\) \((\text{aq}) + e^-\) is a textbook notation for the oxidation of \([\text{EDTA-M}^{(ii)}]^2^-\) complexes in aqueous solutions. As such, the solution phase oxidation potential, \(E_{1/2}\), should have natural connections with the gas phase photodetachment and the 3rd ionization potential (IP) of TM atoms.

The gas phase VDEs of \([\text{EDTA-M}^{(ii)}]^2^-\) \((\text{red and blue triangles})\) are first compared to the 3rd IPs of metal \(\text{M}\) \((\text{green squares})\) in Fig. 6. A reasonable correlation is found between the VDE trend and that of the 3rd IPs for \(\text{M} = \text{V, Cr, Mn, and Fe}\), although their absolute numbers are different. The VDE reaches a plateau at 1.7 eV for the \(\text{M} = \text{Co, Ni, and Cu complexes}\), and 2.0 eV for the \(\text{Zn complex}\), while the 3rd IP of the corresponding metal is seen to continue increasing. The good correlation between the VDE and metal 3rd IP found for the \(\text{M} = \text{V, Cr, Mn, and Fe cases}\) can be qualitatively explained by examining the
HOMO components of these complexes, which shows that the metal core contributes dominantly to each HOMO in the V, Cr, Mn, and Fe complexes (Table 2). In contrast, the ligand EDTA contributes overwhelmingly to each HOMO in the Co, Ni, Cu and Zn EDTA complexes, and therefore exhibits a remarkable non-innocence and modulation ability for the electron removal process,44 a fact that rationalizes the deviation of VDE vs. IP observed in these late TM complexes.

Fig. 6 also compares the solution phase redox potentials $E_{1/2}$ (brown squares)45 with the calculated/experimental VDEs for [EDTA·M(II)]$^{2-}$ (M = V – Co). The overall similarity in the trends of VDE and $E_{1/2}$, which was also reported in several other systems,37,46 suggests that the solvation energies for these quasi-octahedral
structures are similar. A noticeable exception is found for the Co vs. Mn cases, for which $E_{1/2}$ of the Co complex is smaller than that of the Mn complex, but the VDE of the former is higher than that of the latter. A close examination of the HOMO of each complex may provide an explanation. The HOMO of $[\text{EDTA} \cdot \text{Mn(II)}]^2^− \text{Mn(II)}]$ is largely comprised of the metal (50.70%), so the electron removal process can be viewed as $[\text{EDTA} \cdot \text{Mn(II)}]^2^− \rightarrow [\text{EDTA} \cdot \text{Mn(III)}]$. On the contrary, the HOMO of $[\text{EDTA} \cdot \text{Co(II)}]^2^−$ only has a 23% Co contribution, so the electron removal process for this complex is better described as $[\text{EDTA} \cdot \text{Co(II)}]^2^− \rightarrow [\text{EDTA} \cdot \text{Co(III)}]$. It is not surprising that the solvation energy for the Mn(II)/Mn(III) pair is different to that of the EDTA/EDTA$^+$ pair, leading to the observed VDE vs. $E_{1/2}$ deviation for these two complexes. The critical role of solvation energy that could change the VDE vs. $E_{1/2}$ trend over a series of homologues compounds was also reported previously in an investigation of the electronic properties of various functionalized fullerenes.47

Conclusion and perspectives

We have conducted a systematic investigation by employing electrospray ionization PES and quantum computations on a series of divalent metal EDTA complexes $[\text{EDTA} \cdot \text{M(II)}]^2^−$ across the 3rd row metals (M = Ca, V–Zn). The electronic origin of the redox nature of these divalent TM EDTA complexes is unraveled in their PE spectra, in which there is an extra spectral band X with the lowest eBE exhibited, when compared to that of $[\text{EDTA} \cdot \text{Ca(II)}]^2^−$. This X band is largely derived from the metal core for the early TM complexes, with a significant EDTA contribution for the late TM species. Our DFT calculations suggest pseudo-octahedral structures for all complexes, and the calculated VDEs are in good agreement with the experimental measurements. In addition, we compare the gas-phase VDEs with the corresponding solution redox potentials and 3rd IPs of the metals for this series of complexes. Overall, good correlations among these three sets of data are found for the species with their HOMOs largely composed of TMs. Noticeable deviation between the VDEs and IPs occurs when the EDTA ligand significantly contributes to the redox active orbitals, and the VDE–redox potential relationship may break down when the respective solvation energy varies appreciably along the series. In-depth analysis of the results obtained in this work, and those reported in our previous studies, has demonstrated that electrospray ionization PES is indeed a unique ion spectroscopic tool that has a certain predictive power to foresee related redox chemistries over a series of structurally and compositionally similar compounds. However, caution must be practiced in the cases where the solvation energy or the properties of the redox active orbitals change appreciably.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

The experimental work was supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences, and was performed using EMSL, a National
Scientific User Facility sponsored by the DOE’s Office of Biological and Environmental Research, located at Pacific Northwest National Laboratory, which is operated by the Battelle Memorial Institute for the DOE. The computational work was supported by the National Natural Science Foundation of China (Grant No. 21688102) and the Strategic Priority Research Program (Grant No. XDB17000000) of the Chinese Academy of Sciences and was conducted on the clusters at the Center for Theoretical and Computational Chemistry at the Dalian Institute of Chemical Physics.

References