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Energetics of carboxylate-metal bonds in polymetallic rings†

 Niklas Geue,^a Tim Renningholtz,^b George F. S. Whitehead,^b Grigore A. Timco,^b Cristina Trujillo,^b Perdita E. Barran^{*a} and Richard E. P. Winpenny^{*b}

Using collision-induced dissociation mass spectrometry and density functional theory, we assess the energetics of polymetallic $[\text{Cr}_7\text{NiF}_8(\text{O}_2\text{CR})_{16}]^-$ anions *in vacuo*, showing how the carboxylate influences the ring stability. We find the best correlation with the enthalpic contribution to the computed proton affinity of the isolated carboxylates, demonstrating how the stability of polymetallic rings can be predicted *in silico*.

The design of polymetallic complexes has attracted considerable attention over the last decades, with such compounds studied for potential applications in catalysis, extraction, as well as quantum materials.^{1–4} Their synthesis often relies on self-assembly reactions, leading to the formation of energetically stable 2D and 3D structures with fascinating properties.^{2,3} Due to the structural complexity of the complexes and their building blocks, factors governing their stability have rarely been studied which limits a systematic exploitation of these metallosupramolecules.

Mass spectrometry (MS) methods have emerged as powerful tools to understand the structure and properties of large synthetic assemblies, and particularly collision-induced dissociation mass spectrometry (CID-MS) played a major role in this advancement.^{5–7} In CID-MS, ions of interest are isolated through their mass-to-charge (m/z) ratio in a quadrupole mass filter, and subsequently subjected to collisions with an inert gas at user-defined energies.⁸ These collisions commonly induce structural changes and/or fragmentation to smaller ions and neutrals, and the stoichiometry of the fragments, as measured by their mass, can inform on the connectivity and structure of

the precursor ion.⁶ CID-MS is also a powerful tool to measure ions' energetics, which can be quantified through a collision energy ramp. Monitoring the fragment ion intensities at different collision energies can give rise to the median collision energy that is required for fragmentation (E_{50} value, see below), which is comparable across similar ions.^{9,10}

We have been interested in the design of polymetallic chromium rings for over two decades.¹ These molecules have potential applications in quantum computing,¹¹ or in host-guest chemistry¹² and show promise as lithographic resists.¹³ Particularly for the latter, where rapid decomposition of the metal-organic compound is key to high sensitivity of the resist, an understanding of complex stability is important.

From our family of polymetallic rings, the most fundamental structure is $[\text{Cr}_7\text{M}^{\text{II}}\text{F}_8(\text{O}_2\text{CR})_{16}]^-$, in which seven Cr^{III} and one M^{II} centre are arranged in an octagon, and bridged *via* two carboxylate ligands and one fluoride on each edge (Fig. 1 for $\text{M}^{\text{II}} = \text{Ni}^{\text{II}}$).¹ Previously, we have shown that the stability of these $\{\text{Cr}_7\text{M}^{\text{II}}\}^-$ rings strongly depend on the divalent metal M^{II} , and the trends followed arguments from crystal field theory (for 2^- and isostructural $\{\text{Cr}_7\text{M}^{\text{II}}\}^-$ rings with other divalent



Fig. 1 Structure of the polymetallic ring $[\text{Cr}_7\text{Ni}^{\text{II}}\text{F}_8(\text{O}_2\text{CR})_{16}]^-$. (Cr: green, Ni: black, F: yellow, O: red, C: grey).

^a Michael Barber Centre for Collaborative Mass Spectrometry, Manchester Institute of Biotechnology, Department of Chemistry, The University of Manchester, 131 Princess Street, Manchester, M1 7DN, UK. E-mail: niklas.geue@manchester.ac.uk, perdita.barran@manchester.ac.uk

^b Department of Chemistry, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK. E-mail: richard.winpenny@manchester.ac.uk

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Fig. 3 (a) CID-MS spectrum of 2^- ($m/z = 2192$) at $E_{\text{lab}} = 105$ eV. Besides the metastable loss of a methyl group from the carboxylate ligands, the three fragments (i), (ii) and (iii) were found that correspond to the losses of $[\text{Ni}(\text{O}_2\text{CR})_2]$, $[\text{Cr}(\text{O}_2\text{CR})_3]$ and $[\text{Cr}(\text{O}_2\text{CR})_2\text{F}]$, respectively. (b) Normalized survival yield vs. E_{com} fitted to a sigmoidal Hill function, exemplary for 2^- , 7^- and 12^- . The three ions follow the stability (and E_{50} value) order of $2^- > 7^- > 12^-$ (Fig. 2).

Overall, aliphatic carboxylates are more stable than aromatic ligands, however large differences are observed within each group (Fig. 2). We hypothesised that the properties of the free carboxylic acids/carboxylates might determine the relative stability differences between the ring anions. This would enable a computationally inexpensive prediction of polymetallic ring stability *in silico*, facilitating the design of such complexes. Density functional theory (DFT) was used to model several properties, and correlations with the E_{50} value were found for the proton affinity (PA), $\text{p}K_{\text{A}}$ value (in water), the Weizsäcker kinetic energy of the COO^- group in each carboxylate, and the wavenumber of the O–C–O asymmetric stretching vibration (Table S1, ESI †).

The relationship of E_{50} values with PA and $\text{p}K_{\text{A}}$ values follow the argument that more acidic carboxylic acids (lower PA, lower $\text{p}K_{\text{A}}$) result in less basic carboxylates and hence weaker binding to electrophiles such as H^+ , or in the case of the polymetallic rings, Ni^{II} and Cr^{III} . This trend was indeed found for the PA of 1^- – 13^- , however only with $R^2 = 0.33$ after excluding the outlier



Fig. 4 Plot of the enthalpic contributions, ΔE_{cor} , to the proton affinity computed for $\text{RCO}_2^-/\text{RCO}_2\text{H}$ vs. E_{50} values. $R^2 = 0.86$ when excluding the outlier 7^- .

7^- (Fig. S14, ESI †). The correlation with the calculated $\text{p}K_{\text{A}}$ is slightly stronger than the one with PA ($R^2 = 0.59$ with 7^- as outlier, Fig. S15, ESI †). The best correlation is found when only considering the thermal and zero-point energy contributions, ΔE_{cor} , to the PA and neglecting the electronic energy (Fig. 4, see ESI † for definition of ΔE_{cor}). The dominant term in ΔE_{cor} is the change in zero-point energy upon protonation of the carboxylate. It can thus be understood as a measure for the O–H bond strength, where a high ΔE_{cor} indicates a strong O–H bond. This correlates with the stability of the Ni–O and Cr–O bonds (Fig. 4).

In addition to this thermodynamic term, we found a trend between an electron density proxy measure (Weizsäcker kinetic energy) at the carboxylate group and the E_{50} values, with a higher electron density correlated with more stable metal complex (Fig. S16, $R^2 = 0.71$, ESI †). Lower electron density in the carboxylate region will result in weaker bonds to electrophiles such as Ni and Cr, hence agreeing with the E_{50} trend.

This led us to the conclusion that the properties of the isolated carboxylate/carboxylic acid, *i.e.* proton affinity, electron density, vibrational frequencies (Fig. S17, ESI †), are the main factors determining the stability of the entire metal complex. As many factors influence the E_{50} value of an ion, namely the stability of precursor ion, fragment ions and neutral leaving group, as well as number of collisions, site of collision, considerably stronger correlations cannot be expected.

Notably, the ring 7^- is an outlier in most correlation plots (Fig. 4), appearing considerably more stable than predicted by DFT. When modelling the full polymetallic complex 7^- , intramolecular F– π interactions were found between the axial as well as axial and equatorial ligands (Fig. S18, ESI †). These stabilising interactions, which can only occur in 7^- due to the presence of fluorides in the ligands, are likely the source for the increased stability of the complex. Thus, although in most cases the properties of the carboxylate determine the stability of the complex (relative to other carboxylates), exceptions exist for cases where the ligands (de-)stabilise intramolecular interactions as in the case of 7^- . This demonstrates that CID-MS is a



suitable tool for experimentally verifying the DFT stability predictions of such polymetallic rings, and we believe that the methodology presented here can be applied to understand metal–organic binding in metallosupramolecular complexes in general.

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Conflicts of interest

There are no conflicts to declare.

Data availability

Supporting data, containing the raw data of mass spectrometry measurements, were deposited on Figshare (DOI: https://figshare.com/articles/dataset/Supplementary_Dataset_for_the_Energetics_of_Carboxylate-Metal_Bonds_in_Polymetallic_Rings_/28704452?file=54619652). DFT data are available at ioChem-BD (DOI: <https://doi.org/10.19061/iochem-bd-6-515>). CCDC 2431792–2431798 contains the supplementary crystallographic data for the compounds reported in this paper (Table S2 and Fig. S19–S25, ESI†).

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