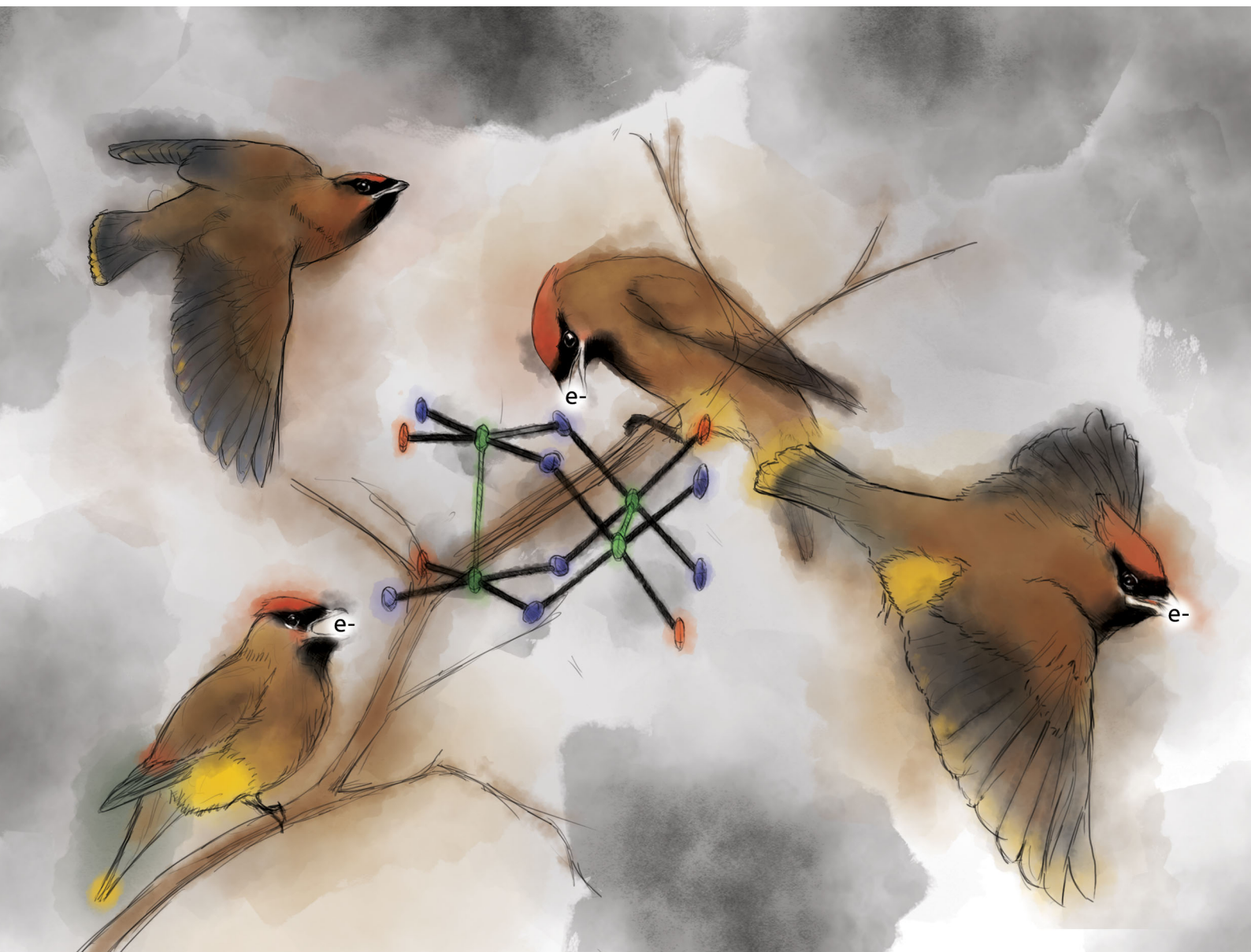


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A tetranuclear nickel cluster isolated in multiple high-valent states†

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We report a series of high-valent tetranuclear nickel clusters isolated from the chemical oxidation of an all Ni(II) ([Ni₄]) neutral cluster. Electrochemical analysis of [Ni₄] reveals three reversible sequential oxidations at 0.248 V (1e[−]), 0.678 V (1e[−]), and 0.991 V (2e[−]) vs. Fc/Fc⁺ corresponding to mono-, di-, and tetra-oxidized species, [Ni₄]⁺, [Ni₄]²⁺, [Ni₄]⁴⁺, respectively. Using spectroscopic, crystallographic, magneto-metric, and computational techniques, we assign the primary loci of oxidations to the Ni centers in each case, thus resulting in the isolation of the first tetranuclear all-Ni(III) cluster, [Ni₄]⁴⁺.

Isolated high-valent nickel complexes (Ni^{III}, Ni^{IV}) are relatively rare,^{1–6} yet are frequently invoked in mechanistic studies involving reductive elimination steps, particularly in C–C and C–heteroatom bond forming chemistry.^{7–10} Bimetallic complexes with formally high-valent cores, [Ni₂]ⁿ⁺ (*n* > 4), have been shown to engage in hydroxylation chemistry, as well as C–heteroatom and N–N bond forming reactions.^{11–14} Co-facial, high-valent (Ni(III)) cores ([Ni₂]⁶⁺) are also proposed to stabilize reactive intermediates through metal–metal bonding interactions,¹⁴ similar to more extensively studied heavier [Pd₂] congeners.^{15,16} Co-facial bimetallics have also been extensively studied by Cotton and others¹⁷ using the familiar C₄-symmetric paddlewheel geometries, including in mixed-valent ([Ni₂]⁵⁺) and all high-valent ([Ni₂]⁶⁺) cores, providing significant fundamental insights into Ni–Ni bonding interactions.^{18,19} While multinuclear Ni complexes ([Ni_x]; *x* > 2) are well known^{20–24} – with some isolated in partial higher-valent states^{25–28} – to the best of our knowledge, only a few are isolated in all Ni(III) states,^{29,30} and none are tetranuclear. Tethering multiple high-valent centers together may open the door to mediating multi-electron transformations, and

may further shed light on core metal–metal bonding interactions in such expanded motifs. Herein, we describe the synthesis and characterization of a tetranuclear [Ni₄]⁸⁺ cluster (denoted [Ni₄]; Scheme 1), with an orthogonal double paddle

In order to target higher nuclearity complexes, we modified a known, dinucleating, xanthene-bridged bis-salen ligand³¹ by exposing its precursor, 5,5'-(9,9-dimethylxanthene-4,5-diyl)bis-(salicylaldehyde), to an excess (10×) of 1,2-diaminobenzene in ethanol under reflux. The product ligand, **LH₄** (Scheme 1), was cleanly generated in 84% isolated yield following workup and now features two tridentate pockets, making it more amenable to cluster formation. Metalation of **LH₄** with 2 equiv. of Ni(OAc)₂·4H₂O afforded the tetranuclear complex, **L₂Ni₄** (**[Ni₄]**), in 50% isolated yield following workup (Scheme 1). The red, diamagnetic, air stable complex was readily characterized by ¹H NMR spectroscopy and MALDI mass spectrometry. Red single crystals suitable for X-ray diffraction (XRD) studies were grown by vapor diffusion of hexanes into a concentrated dichloromethane (DCM) solution. The solid-state molecular structure revealed four Ni centers in square planar geometries with the fourth coordination sites filled by amine donating groups from adjacent ligands (Scheme 1 and Fig. 1a, Fig. S15, ESI†). The tetranuclear core features co-facial Ni1–Ni2 and Ni3–Ni4 distances of 2.8662(19) Å and 2.886(2) Å, respectively, and adopts an orthogonal double paddlewheel structure (Fig. 1a and Table 1). The transverse Ni–Ni distances (e.g. Ni₁–Ni₃) are longer and average 3.33 Å.

Cyclic voltammetry (CV) of **[Ni₄]** in 1,1,2,2-tetrachloroethane (TCE) revealed three reversible oxidation events at *E*_{1/2} values of 0.248, 0.678, and 0.991 V *versus* the ferrocene/ferrocenium (Fc/Fc⁺) redox couple (Fig. 1b) in approximate 1:1:2 e[−] events, respectively, as determined by relative integrations of the oxidative curves. Chemical isolation of the mono-oxidized product was performed by treatment of **[Ni₄]** with an equivalent of [NO][PF₆] to yield **[L₂Ni₄][PF₆]** (**[Ni₄]⁺**; Scheme 1). Single crystals suitable for XRD studies were obtained by layering hexanes on a concentrated DCM solution of **[Ni₄]⁺** at −40 °C. The solid-state structure revealed a significantly contracted Ni3–Ni4 distance of 2.640(2) Å, and a relatively unperturbed Ni1–Ni2 distance of 2.889(2) Å, identical within error to the Ni3–Ni4 bond in **[Ni₄]** (Fig. S16, ESI† and Table 1). Corresponding protrusions of the Ni centers relative to their respective mean tridentate ligand planes (excluding bridging donor atom from an adjacent ligand) are consistent with the bond length contraction (Table 1 and Fig. S23, ESI†). The significant shortening of the Ni3–Ni4 distance is consistent with the formation of a long, formal half bond expected from the

removal of a single e[−] from an *e*-symmetric σ* orbital located along the Ni3–Ni4 vector (Fig. 1c),^{18,19,32} using a simplified *D*_{2d}-symmetric tetranuclear model and ignoring extensive ligand π mixing. An overall spin of $\frac{1}{2}$, determined by the Evans method, further confirmed this assignment.³³ In addition, analysis of **[Ni₄]⁺** by EPR spectroscopy in DCM at 100 K revealed a rhombic spectrum with significant *g* tensor anisotropy modeled as: *g*_x = 2.01, *g*_y = 2.22, *g*_z = 2.32, and *g*_{av} = 2.18 (Fig. S12, ESI†), consistent with previously reported Ni-centered oxidation events.^{3,4,19} While the UV-Vis absorption spectrum of **[Ni₄]⁺** is similar to **[Ni₄]**, a distinct absorption in the NIR at 1300 nm (*ε* = 3277 M^{−1} cm^{−1}) is observed for **[Ni₄]⁺** (Fig. S11, ESI†) which we tentatively assign as a charge transfer band (based on its high *ε*),^{19,34} likely lig

Table 1 Ni–Ni and Ni–mean plane distances obtained from single-crystal XRD studies

		[Ni ₄]	[Ni ₄] ⁺	[Ni ₄] ²⁺	[Ni ₄] ⁴⁺
Ni–Ni distance (Å)	Ni1–Ni2	2.8662(19)	2.889(2)	2.7095(18)	2.686(3)
	Ni3–Ni4	2.886(2)	2.640(2)	2.6284(18)	2.668(3)
	Avg	2.876	2.765	2.669	2.677
Ni–mean plane distance (Å)	Ni1	0.065	0.090	0.114	0.123
	Ni2	0.055	0.073	0.139	0.123
	Ni3	0.080	0.158	0.140	0.143
	Ni4	0.064	0.117	0.130	0.143
	Avg	0.066	0.110	0.131	0.133

through the bridging nitrogen atoms. This degree of magnetic exchange in polynuclear high-valent Ni species *via* super exchange is not unprecedented and even greater magnitudes have been reported.³⁰ The absorption spectrum revealed a red-shifted LMCT absorbance at 1410 nm ($\epsilon = 14\,574\text{ M}^{-1}\text{ cm}^{-1}$) in the NIR, the intensity of which is over four times as intense as the one in [Ni₄]⁺ (Fig. S11, ESI†). Lastly, a K_c value of $\sim 2 \times 10^5$, obtained from the difference in the two highest $E_{1/2}$ values,³⁵ suggests a more localized electronic structure consistent with a Robin-Day Class II system.

The isolation of the tetra-oxidized species was achieved by treating [Ni₄] with 10 equiv. of [(2,4-Br₂C₆H₃)₃N][B(C₆F₅)₄] to yield [L₂Ni₄][B(C₆F₅)₄]₄ ([Ni₄]⁴⁺; Scheme 1). Single crystals suitable for XRD studies were obtained by layering hexanes on a concentrated DCM solution of [Ni₄]⁴⁺ at -40°C . Similar to [Ni₄]²⁺, both Ni–Ni distances are contracted relative to [Ni₄], and concurrent protrusions of the Ni centers from the mean ligand tridentate planes are observed (Table 1 and Fig. S18, S23, ESI†). However, these effects are less pronounced than in the dicationic [Ni₄]²⁺, and we attribute this distinction to the increased electrostatic repulsion between cationic metal centers in [Ni₄]⁴⁺ relative to [Ni₄]²⁺.^{17,37} Attempts to obtain magnetic measurements of [Ni₄]⁴⁺ were hampered by its extreme instability (*vide infra*). Nonetheless, the ¹H NMR spectrum of *in situ*-generated [Ni₄]⁴⁺ revealed a paramagnetic species (Fig. S9, ESI†), likely arising from thermal population of a higher spin state (Fig. 1c). The absorption spectrum of *in situ*-generated [Ni₄]⁴⁺ revealed an intense ($\epsilon = 22\,099\text{ M}^{-1}\text{ cm}^{-1}$) red-shifted LMCT band in the NIR

bonds upon oxidation – expected from metal-based oxidations^{3,19} – but no discernable bond change patterns within the ligand π framework expected from ligand-based oxidation (Table S1 and Fig. S19–S22, ESI†). With this, and together with our combined experimental and theoretical results above, we propose that $[\text{Ni}_4]$ undergoes primarily metal-based oxidation events.

In conclusion, a novel tetranuclear Ni species isolated in multiple high-valent states, including an all Ni(III) state, is reported and supported by spectroscopic, crystallographic, magnetometric, and computational data. We are currently investigating potential applications of this cluster in mediating multi-electron transformations at small molecules of energy importance.

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Conflicts of interest

There are no conflicts to declare.

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