Study of Electronic and Vibrational Structures of Reduced, Neutral, and Oxidized Ni$_3$(dpa)$_4$X$_2$ Using Density Functional Theory and Raman Spectroscopy

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1. INTRODUCTION

The trinuclear metal complexes M$_3$(dpa)$_4$X$_2$ (dpa = dipyridyl amido, M = Ni, Co, Cu, Cr, Rh, and Ru, etc., X = Cl, NCS) are the simplest extended metal atom chains (EMACs). The purple complex Ni$_3$(dpa)$_4$Cl$_2$ was first synthesized by Hurley and Robinson, and Hathaway et al. determined that its structure has a collinear metal chain, coordinated by equatorial ligands (dpa$^-$), as shown in Scheme 1. The bond lengths between metals are d$_{Ni−Ni}$ = 2.42−2.44 Å, and those of the terminal nickels to equatorial ligands are d$_{Ni(term)−N}$ = 2.08−2.10 Å. The proton NMR spectra showed this complex to have D$_4$ symmetry in solution. According to the delocalized molecular orbital (DMO) theory, Clerc et al. proposed that this complex, which has a [Ni$_3$$^{6+}$] core, possesses 24 valance electrons to fill all bonding, nonbonding, and antibonding MOs of $\sigma$, $\pi$, and $\delta$. This yielded a symmetric structure and no Ni−Ni bonds, resulting in large bond lengths between metal ions. However, they proposed that in this complex the terminal Ni$^{2+}$ each has two unpaired electrons (high-spin, $S_t = 1$), while the central one is diamagnetic (low-spin, $S_c = 0$). Peng et al., according to the results of X-ray absorption measurements, confirmed this antiferromagnetic (AF) structure—a singlet ground state (GS). The results of magnetic susceptibility measurements showed an AF exchange constant $J_{ab}$ of about $-108$ cm$^{-1}$. These structures and magnetic properties were confirmed and discussed by many research groups using density functional theory (DFT) calculations.

Berry et al. oxidized [Ni$_3$]$^{6+}$ to [Ni$_3$]$^{7+}$ to produce [Ni$_3$(dpa)$_4$]$(PF_6)_3$ without axial ligands, in which d$_{Ni−Ni}$ is decreased to 2.28 Å, and suggested that this complex had a three-center metal−metal bond. Thus, the large contraction in metal bond length might be applied to the molecular switch by manipulation of the electrode potentials. Kiehl et al. investigated the electronic structure with density functional

Scheme 1. Structures of (1) Ni$_3$(dpa)$_4$Cl$_2$, (2) Ni$_3$(dpa)$_4$(NCS)$_2$, (3) H$_2$BPAP, and (4) H$_2$phdpda
theory (DFT) generalized gradient approximation (GGA) functional BP86 and hybrid functional B3LYP. The exchange constant $J_{ab}$ and the electronic structure of Ni$_3$(dpa)$_4$Cl$_2$ were calculated using the broken-symmetry (BS) method; the values of $J_{ab}$ were $-55$ and $-322$ cm$^{-1}$ with B3LYP and BP86, respectively. They showed that the AF ground state of Ni$_3$(dpa)$_4$Cl$_2$ has $\sigma$ bonding character with a bond order (BO) equal to 0.5. In addition, the large contraction of $d_{N\xi-N\xi}$ for [Ni$_3$]$^{3+}$ converted to [Ni$_3$]$^{2+}$ was obtained, and they proposed that it was the trans effect, resulting from the vanishing of the axial ligands. Likewise, Kitagawa et al. 23 suggested that it was due to the vanishing of the axial ligands. In this state, two electron spins are antiparallel, leading to a singlet ground state ($S = 0$) of Ni$_3$(dpa)$_4$Cl$_2$ were calculated using the DFT methods BP86, B3LYP*, and B3LYP*-D3. Table 3 lists the bond distances connected to metals, the spin distribution, and the exchange constant. According to the molecular orbital theory, the $z$-axis was assumed to be along the metal chain and the $x$- and $y$-axes were along the directions of metal bonds to equatorial ligands. The $d_{x^2}$ orbitals of three metal ions were linearly combined to form the $\sigma$ molecular orbitals (MOs), namely, bonding, nonbonding, and antibonding orbitals; the $d_{yz}$, $d_{xz}$, and $d_{xy}$ formed $\pi$- and $\delta$-type MOs, and the $d_{x^2-y^2}$ was used to bond with equatorial ligands.

We obtained large bond distances of Ni–Ni in the AF ($S = 0$) state, indicating poor overlap of the adjacent Ni d orbitals. From the calculated MOs, the individual metal d electrons were more localized, resulting in the terminal nickel forming five-coordinated square pyramids with antiferromagnetic coupling and a localized central nickel forming an isolated four-coordinate square plane. Based on the bond structures of nickel ions, these MOs can be roughly divided into three subcomplexes, as shown in Figure 1: (1) two square-pyramidal terminal nickel ions: the $d_{e_1}$ and $d_{e_2}$ orbitals bonded with axial ligands, $d_{e_3}$ formed a nearly nonbonding orbital, and $d_{t_2}$ and $d_{d}$ formed antibonding orbitals with equatorial ligands and axial ligands, respectively, and (2) one square-planar central nickel ion: the $d_{x^2-y^2}$ formed the antibonding orbital with equatorial ligands, and the other d orbitals formed nonbonding orbitals. This formed a typical localized MO (LMO) model for the EMAC.

This AF state was calculated as $d_{N-Ni} = 2.4231$ and 2.4672 Å and $d_{Ni-Cl} = 2.3510$ and 2.3691 Å using the BP86 and B3LYP* methods, respectively. The optimized geometries obtained from BP86 were closer to the experimental data. However, BP86 yielded a much smaller exchange constant $J_{ab} = -296.7$ cm$^{-1}$ than the B3LYP* value $J_{ab} = -96.98$ cm$^{-1}$, which was closer to the experimental value $-108$ cm$^{-1}$. Considering the effect of noncovalent interactions, we employed a dispersion correction D3 to include the van der Waals interactions between metals; B3LYP*-D3 yielded a slightly smaller bond distance and exchange constant: $d_{N-Ni} = 2.4281$ Å and $J_{ab} = -116.73$ cm$^{-1}$, which were in satisfactory agreement with the experimental values (Table 1). Therefore, we employed this theoretical method to the other electronic states and also to calculate the Raman bands to verify the vibrational structures. Complex with axial ligand NCS has a similar geometry and spectral properties, hence, the NCS results are not discussed here.

For the quintet state, we obtained $d_{N-Ni} = 2.4418$ Å and $d_{Ni-Cl} = 2.3419$ Å, which lie 8.38 kJ mol$^{-1}$ above the AF state. In this state, two electron spins are flipped on a terminal nickel to have the total spin $S = 2$. Similar to the AF state, the quintet state displayed a LMO type of metal bonding, yielding little bonding between nickel ions but the metal to the axial ligand Ni-Cl was in bonding conditions. The singlet diamagnetic state, which lies 115 kJ mol$^{-1}$ above the calculated MOs, appeared to be a delocalized MO (DMO) type, as shown in Figure 2. Thus, a shorter Ni–Ni bond distance $d_{N-Ni} = 2.3804$ Å and a long $d_{Ni-Cl} = 2.8641$ Å were attained; the bonding between Ni and Cl was antibonding. Kiehl et al. 22 suggested a large $d_{Ni-Cl}$ like a dissociated trend for axial ligands, leading to a trans effect with large contraction of the Ni–Ni distance and the transfer of electronic density shield electrostatic repulsion between nickel atoms. In comparison with other complexes without axial ligands, such
Table 1. Properties of AF, Quintet, and Diamagnetic Singlet States of Ni₃(dpa)₄Cl₂, and Singlet [Ni₃(dpa)₄]²⁺ Calculated by Various DFT Methods

| Method | Distance (Å) | Spin Distribution | ΔEₜₙ (kJ mol⁻¹) | MO type | Ref. |
|--------|--------------|-------------------|-----------------|---------|------|
| BP86   | 2.4321       |                  | 2.2109          | localized | 28   |
|        | 2.3510       |                  | 2.4193          | localized | 28   |
|        | 2.0971       |                  | 1.9264          | localized | 28   |
|        | 1.9227       |                  | 1.9201          | localized | 28   |
|        | 1.8994       |                  | 1.8994          | localized | 28   |
| B3LYP  | 2.4418       |                  | 2.4418          | localized | 28   |
|        | 2.4418       |                  | 2.4418          | localized | 28   |
|        | 2.4418       |                  | 2.4418          | localized | 28   |
|        | 2.4418       |                  | 2.4418          | localized | 28   |
|        | 2.4418       |                  | 2.4418          | localized | 28   |
|        | 2.4418       |                  | 2.4418          | localized | 28   |

as [Ni₃(BPAP)₄]²⁻ (BPAP = 2,6-bis(phenylamino)pyridine, Scheme 1), the measured dₙ-Ni = 2.368 Å, similar to the calculated value for the diamagnetic singlet state. However, we calculated the ground-state geometry of [Ni₃(dpa)₄]²⁺ and obtained dₙ-Ni = 2.3218 Å, about 0.06 Å less; this is in some way a significant difference. Lai et al. synthesized a complex [Ni₄(μ₃-phdpda)₄] (phdpda = N-phenylpyridylidiamine, Scheme 1) with dₙ-Ni = 2.30–2.32 Å. Upon comparing these three ligands, dpa⁻ was found to be close to phdpda⁻ in terms of rigidity to constrain metal ions. The calculated dₙ-Ni of [Ni₃(dpa)₄]²⁺ was near that of [Ni₄(μ₃-phdpda)₄], indicating that our calculated geometry using B3LYP*-D3 for the cation was reliable. These geometric values are listed in Table 1.

The MOs of the singlet diamagnetic state of Ni₃(dpa)₄Cl₂ and [Ni₃(dpa)₄]³⁺ followed the DMO model. However, in these states, the d electrons filled up all three metal-center orbitals, resulting in BO = 0 in metal bonds, and the contraction of the metal—metal distance mainly resulted from the vanishing of the axial ligands. In contrast, the MOs of the quintet and the AF states followed the LMO model, which displayed the nearly detached metal ions.

2.1.2. [Ni₃(dpa)₄X₂]⁺ and [Ni₃(dpa)₄]³⁺. Table 2 lists the calculated geometries and the spin distributions of the two lowest energy spin states of [Ni₃(dpa)₄Cl₂]⁺ and [Ni₃(dpa)₄]³⁺ with [Ni₃]³⁺ cores. The results of B3LYP*-D3 yielded a doublet ground state for [Ni₃(dpa)₄]³⁺, which was less by 68.4 kJ mol⁻¹ in energy than the quartet state; the dₙ-Ni was further contracted to 2.2816 Å and the central d Ni(term) was slightly increased to 1.8891 Å, in agreement with the experimental geometry. This cation without axial ligands followed a DMO-type model with an electron configuration of (σ*)²(σnb)², corresponding to a 2A₁ state. Its quartet state had a slightly shorter dₙ-Ni = 2.2664 Å but a longer d Ni(center) = 1.9861 Å, also with DMO-type bonding and an electron configuration of (σ*)²(σnb)²(δ*(b)²). For [Ni₃(dpa)₄Cl₂]⁺, B3LYP*-D3 showed a quartet state that was lower in energy from the doublet state by 10.2 kJ mol⁻¹, in contrast to the results of Kiehl et al. using the BP86 method, they reported a doublet ground state. The quartet state has a LMO-type bond, removing just one electron from the dₙ-Ni orbitals of the quintet state of Ni₃(dpa)₄Cl₂. Hence, similarly, a long dₙ-Ni = 2.4413 Å was obtained. However, the doublet state has a DMO and an electron configuration of (σ*)²(σnb)²(σ*)², as shown in Figure 3; thus, a short dₙ-Ni = 2.3528 Å. A large energy split in the σ MOs resulted from a large Ni–Ni overlap and the σ* orbital lies near the antibonding MO δ*(Ni-term)–N. Here, the σ orbital exhibited bonding in both Ni–Ni and Ni–Cl, but Kiehl et al. showed antibonding in Ni–Cl instead. In addition, our calculations showed that both σ* and σnb displayed antibonding in Ni–Cl; hence, dₛ-Ni = 2.5339 Å, which is relatively long. Unfortunately, no crystal structure has been reported for this unstable complex [Ni₃(dpa)₄Cl₂]⁺ to verify the theoretical argument on the spin state. Nevertheless, spectroscopic techniques such as electronic structures and Raman spectra can be used to elucidate this issue.

2.1.3. [Ni₃(dpa)₄X₂]⁺. Table 3 displays the optimized geometries of the lowest energy doublet and quartet states of [Ni₃(dpa)₄X₂]⁺, X = Cl and NCS. For both axial ligands, the quartet state is the ground state with dₛ-Ni = 2.42 Å, dₙ-Ni(term) = 2.10 Å, and dₙ-Ni(center) = 1.91–1.92 Å. Its molecular orbitals are localized, and the structures possess D₄₃d symmetry.
Figure 1. Molecular orbital diagram of Ni₃(dpa)₄Cl₂ for the AF broken-symmetry state displaying a local molecular orbital (LMO) type of bonding.

Figure 2. Molecular orbital diagram of the closed-shell singlet diamagnetic state of Ni₃(dpa)₄Cl₂ displaying a delocalized molecular orbital (DMO) type of bonding.

Table 2. Properties of Doublet and Quartet States of [Ni₃(dpa)₄Cl₂]⁺ and of [Ni₃(dpa)₄]³⁺, Calculated Using the DFT Method B3LYP*-D3

|                     | [Ni₃(dpa)₄Cl₂]⁺ | [Ni₃(dpa)₄]³⁺ |
|---------------------|-----------------|---------------|
| Distance Ni–Ni      | 2.3528          | 2.4413        |
| Ni–Cl               | 2.5339          | 2.3094        |
| Ni₃axial–N          | 1.9693          | 2.1083        |
| Ni₃merid–N          | 1.8819          | 1.8942        |
| spin distribution   |                 |               |
| Ni(1)               | 0.2624          | 0.1892        |
| Ni(2)               | 0.3164          | 0.14266       |
| Ni(3)               | 0.2624          | 0.1892        |
| ΔE (kJ mol⁻¹)       | +10.2           | 0             |
| MO type             | delocalized     | localized     |

Ref 9.
symmetry. The extra electron of the reduced form filled in the antibonding orbital of Ni–Cl, yielding a long dNi–Cl = 2.5266 Å. For the excited state (ES), two doublet states were found: one C4 and the other D4 symmetry. The C4 doublet state is also a broken-symmetry state with LMO bonding, and its electron configuration differs from the quartet state by flipping an electron in the terminal d$x^2$−$y^2$ orbital, as shown in Figure 4. According to the calculations, for axial ligand Cl, this doublet state lies 22.8 kJ mol$^{-1}$ above the ground state for axial ligand NCS 22.5 kJ mol$^{-1}$. However, the D4 doublet state followed a DMO-type metal bonding. One more electron filled the terminal $δ^{\ast}$Ni–N, resulting in a longer distance of dNi(term)–N = 2.0213 Å, a slightly short dNi–Ni = 2.4070 Å, and a very long dNi–Cl = 2.9030 Å. This highly symmetric doublet state lies at an energy of 126 kJ mol$^{-1}$ and, hence, is for sure an excited state.

### 2.2. Electronic Transitions and Vibrational Spectra.

#### 2.2.1. Ni$_3$(dpa)$_4$X$_2$.

Figure 5a shows the measured steady-state absorption spectra of Ni$_3$(dpa)$_4$Cl$_2$ and Hdpa. The complex had a visible band at 528 nm and a shoulder band at 630 nm. The results of time-dependent (TD) DFT calculations are depicted in Figure 5b, showing the 13th (S13) and 21st (S21) vertical transitions of 607 and 528 nm, respectively, consistent with the experimental results in the visible range. The band characters analyzed by the IFCT method for each excited transition are listed in Table S1. Most vertical transitions with oscillator strengths were from the equatorial ligands and/or the metal ions rather than the axial ligands, resulting in similar visible absorption spectra of complexes with various axial ligands. The band at 630 nm (607 nm cal.) was assigned to d$x^2$−$y^2$→d$x^2$−$y^2$ of the central nickel, a localized d−d transition, and the band at 528 nm was assigned to d$x^2$→d$^{\ast}$−$y^2$ of the central nickel, plus some ligand-to-metal charge transfer.

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**Table 3. Properties of Doublet and Quartet States of [Ni$_3$(dpa)$_4$Cl$_2$]$^{-}$ Calculated Using the DFT Method B3LYP*-D3**

| [Ni$_3$]$^{\cdot\cdot\cdot}$ | [Ni$_3$(dpa)$_4$Cl$_2$]$^{-}$ | [Ni$_3$(dpa)$_4$(NCS)$_2$]$^{-}$ |
|---------------------------|-----------------------------|-------------------------------|
| point group | D$_4$ | C$_4$ | D$_4$ | C$_4$ | D$_4$ |
| Ni(1)–Ni(2) | 2.4070 | 2.4301 | 2.4208 | 2.4339 | 2.4237 |
| Ni(2)–Ni(3) | 2.4070 | 2.4140 | 2.4208 | 2.4124 | 2.4237 |
| Ni(1)–Cl/N(CS) | 2.9030 | 2.6504 | 2.5266 | 2.1147 | 2.0837 |
| Ni(3)–Cl/N(CS) | 2.9030 | 2.4563 | 2.5266 | 2.0448 | 2.0837 |
| Ni$_{term}$–N | 2.0153 | 2.1079 | 2.1062 | 2.1025 | 2.1016 |
| Ni$_{center}$–N | 1.9150 | 1.9155 | 1.9148 | 1.9191 | 1.9186 |
| Spin distribution | | | | | |
| Ni(1) | 0.4729 | -0.7242 | 1.2308 | -0.7332 | 1.2422 |
| Ni(2) | 0.0187 | 0.1699 | 0.1282 | 0.1660 | 0.1166 |
| Ni(3) | 0.4729 | 1.3867 | 1.2308 | 1.4066 | 1.2422 |
| $ΔE$ (kJ mol$^{-1}$) | +126 | +22.8 | 0 | +22.5 | 0 |
| MO type | delocalized | localized | localized | localized | localized |

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Figure 4. Electron configuration of (a) the doublet (C$_4$) and (b) the quartet states of [Ni$_3$(dpa)$_4$X$_2$]$^{-}$. 

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Figure 3. Molecular orbital diagram of the open-shell doublet state of [Ni$_3$(dpa)$_4$Cl$_2$]$^{\cdot\cdot\cdot}$ displaying a DMO type of bonding.
(LMCT) character. Figure S1 shows the hole–electron distributions of these S13 and S21 transitions. Bands of less than 400 nm corresponded to the π→π* of the equatorial ligands, which confirmed the experimental assignments of Cheng et al. in that excitation in the ultraviolet and visible bands accessed the ligand and metal moieties, separately. Table 4 lists the experimental and calculated electronic bands and their assignments.

Based on the results of calculations, the metal–metal bond in this neutral Ni3 complex is weak; therefore, the Raman band of the Ni3 symmetry stretch has insufficient strength to show intensity. In contrast, the bonding character in Ni–Cl resulted in a moderate Raman intensity of the Ni–Cl stretch νNi–Cl.

Figure 6 presents the experimental (Figure 6a,c–g) and the calculated (Figure 6b,h) Raman spectra of Ni3(dpa)4X2 in the wavenumber range of 150–450 cm−1 and the assignments. The experimental curves measured at ∼297 K are displayed in Figure 6a,e for X = NCS and Cl, respectively; they display similar spectra, except for the 287 and 282.5 cm−1 bands. According to the calculations, the band of υNi–Cl of the AF state is at 291 cm−1 and that of υNi–N(NCS) is at 295 cm−1, and the other band positions are almost unaltered (the differences are within 1 cm−1). For the first time, the calculated curves, particularly for the metal-related vibrational modes, agreed with the experimental observation for EMACs. The other assignments based on the calculated vibrational modes are displayed in Figure 6h; the metal-related stretching and bending and the motions involving pyridyl–pyridyl are in this wavenumber range. We assigned the measured bands of Figure 6a,e for X = NCS and Cl, respectively; they display similar spectra, except for the 287 and 282.5 cm−1 bands.

According to magnetic susceptibility measurements, the quintet state gained population with temperature. Upon flipping of the electron spin in the terminal nickel to convert to the quintet state, the vibrational structure was almost unaltered; only υNi–Cl slightly increased from 291 to 294 cm−1 in the calculations, as shown in Figure 6b,h. To resolve this quintet state, we applied a magnetic field of ≈2400 Gauss and a high-resolution grating to the Raman setup and tried to observe the variation due to the quintet state when the...
temperature was changed from 77 to 623 K, as shown in Figure 6c–g. At 77 K, the experimental spectra showed \( \nu_{\text{Ni}-\text{Cl}} = 282.5 \text{ cm}^{-1} \); they were red-shifted to 280.7 cm\(^{-1}\) at 623 K without a magnetic field (as shown in Figure S2), and the red shift is due to a thermal shift. But this band blue-shifted to 283.8 cm\(^{-1}\) (Figure 6c) under 2400 Gauss, about 3.1 cm\(^{-1}\) variation. The other bands were nearly unaltered or had similar shifts as in the no magnetic field conditions. This agreed with the calculation of a 3 cm\(^{-1}\) blue shift for conversion to the quintet state. Conclusively, the AF and the quintet states have almost identical vibrational structures, except for the minor variation in Ni–Cl bond. The weak metal–metal bonds in the trinickel complex yielded no Raman intensity to verify the slightly varied Ni–Ni bond distances between them. However, the quintet state existed and laid at slightly higher energy above the AF ground state.

2.2.2. \([\text{Ni}_3(\text{dpa})_4X_2]^+\) and \([\text{Ni}_3(\text{dpa})_4]^3+\). The electrochemical absorption spectra of \([\text{Ni}_3(\text{dpa})_4X_2]\) \(X_2\) were recorded for the electric potential of –1.3 to +1.3 V (vs Ag/AgCl) to attain the reduced and the oxidized forms (as shown in Figure S3). The bands of \([\text{Ni}_3]^7+\) appearing at 620–630 nm were consistent with the electrochemical measurements of Yeh et al.\(^{32}\) except that they observed an extra weak band at 1065 nm in the near-infrared (IR) region. Berry et al.\(^{33}\) showed \([\text{Ni}_3(\text{dpa})_4]^3+\) \((\text{PF}_6^-)_2\) to have an intense electronic band at 580 nm and a weak one at 1045 nm. According to our TD-DFT calculations, we obtained the vertical transitions of the doublet ground state of \([\text{Ni}_3(\text{dpa})_4]^3+\) at 592 nm, attributed to a \(\sigma \rightarrow \sigma^*\) (d–d) transition, and 1019 nm, attributed to a LMCT transition. These agreed with the experimental observation. Figure S4 displays the calculated absorption spectra, the hole–electron distribution, and the results of IFCT analysis. However, the observed bands at 620–630 nm for the \([\text{Ni}_3]^7+\) core differed from the observation of Berry et al.\(^{33}\) for \([\text{Ni}_3(\text{dpa})_4]^3+\) and possibly can be attributed to \([\text{Ni}_3(\text{dpa})_4X_2]^+\).

The calculated vertical transitions of doublet \([\text{Ni}_3(\text{dpa})_4\text{Cl}_2]^+\) were 615, 851, and 1452 nm, as shown in Figure S5, which disagreed with experimental observations. The intense band at 851 nm (the 12th transition) was assigned to the \(\sigma \rightarrow \sigma^*\) (d–d) transition, and particularly, the MOs of the axial ligands participated in this electronic transition. The antibonding in Ni–Cl resulted in destabilization of the \(\sigma_{ab}\) orbital; therefore, this band was red-shifted to 851 nm. The 4th (1452 nm) and the 37th (615 nm) vertical transitions (S4 and S37) were assigned to d–d transitions mixed with LMCT and \(\delta^* \rightarrow \delta^*\) respectively (Figure S5). For quartet \([\text{Ni}_3(\text{dpa})_4\text{Cl}_2]^+\), the main transition was calculated to be at 645 nm, the 28th transition, and assigned to an intraligand charge transfer mixed with partial \(\pi \rightarrow \pi^*\) transition, as shown in Figure S6. However, this quartet state showed no corresponding transition with oscillator strength in the near-IR region. Combining both experimental and theoretical data, we tentatively assigned the electrochemical absorption band at 1065 nm to doublet \([\text{Ni}_3(\text{dpa})_4]^3+\), which had a calculated near-IR band at 1019 nm. The visible band near 634 nm was assigned to quartet \([\text{Ni}_3(\text{dpa})_4\text{Cl}_2]^+\) + doublet \([\text{Ni}_3(\text{dpa})_4]^3+\). Therefore, the calculated results of B3LYP*–D3 yield the correct ground state: quartet \([\text{Ni}_3(\text{dpa})_4\text{Cl}_2]^+\) and doublet \([\text{Ni}_3(\text{dpa})_4]^3+\). During oxidation processes, the doublet \([\text{Ni}_3(\text{dpa})_4\text{Cl}_2]^+\) was unobserved in these reactions and should be an excited state.

Figure 7a,b presents the SERS spectra of the \([\text{Ni}_3]^7+\) core measured immediately upon addition of oxidant AgPF\(_6\) and about 1–2 min later, respectively. The calculated Raman spectra of quartet \([\text{Ni}_3(\text{dpa})_4\text{Cl}_2]^+\) and doublet \([\text{Ni}_3(\text{dpa})_4]^3+\) are shown in Figure 7c,d, respectively. The band appearing at 350 cm\(^{-1}\) and shifted to 355 cm\(^{-1}\) later in the experimental curves was reassigned to the out-of-plane deformation mode of pyridyl rings; this mode was calculated to be 375 cm\(^{-1}\) for \([\text{Ni}_3(\text{dpa})_4\text{Cl}_2]^+\) and 355 cm\(^{-1}\) for doublet \([\text{Ni}_3(\text{dpa})_4]^3+\). Unfortunately, the calculated band position for the Ni\(_3\) symmetric stretching \(\nu_{\text{Ni}_3\text{sym}}\) of \([\text{Ni}_3(\text{dpa})_4]^3+\) was 289 cm\(^{-1}\), but this band was overlapped with the solvent band (dichloromethane). This made it hard to differentiate these complexes solely based on the SERS spectra. Nevertheless, in the oxidation process, both complexes can be formed, and this is consistent with the conclusion drawn based on the electronic spectra.

2.2.3. \([\text{Ni}_3(\text{dpa})_4X_2]^+\). Both TD-DFT calculations on the \(D_4\) quartet and \(C_4\) doublet states of \([\text{Ni}_3(\text{dpa})_4X_2]^+\) yielded several vertical transitions in the range of 500–600 nm, and a single transition at 1040 nm. For both states, the near-IR band at 1040 nm has a large oscillator strength, and the band was assigned to a d\(^{2}\)–d\(^{2}\) charge transfer between two terminal Ni–Cl, as shown in Figure S7. Our experimental data obtained in the visible range only yielded a broad band centered at 500 nm. Hence, based on the electronic spectra alone, these two spin states are indistinguishable.

Figure 8a displays the Au-SERS spectra for the \([\text{Ni}_3]^3+\) core, complex \([\text{Ni}_3(\text{dpa})_4(\text{NCS})_2]^2+\); the SERS sample was dripped onto a quartz cell and dried under vacuum, and then the temperature was varied in the range of 77–623 K. Figure 8b displays the calculated Raman spectra for the doublet \(C_4\) state and the quartet state, respectively. Complex \([\text{Ni}_3(\text{dpa})_4X_2]^+\) was reduced by the AuNP when attached to a gold nanoparticle surface. According to the calculated MOs and geometries, the two spin states of the reduced form follow the LMO type of bonding and exhibit less metal–metal bonds. In the calculated spectra, the most obvious difference was the Ni–N(CS) stretching modes, which lie at 230/244 and 236 cm\(^{-1}\) for the doublet \((C_4)\) and quartet states \((D_4)\), respectively. From the
temperature-dependent SERS spectra, the 242 cm$^{-1}$ band appeared to start from 113 K and increased in intensity with temperature. Accordingly, we assigned this band to the second $\nu_{Ni-N(CS)}$ (cal. 244 cm$^{-1}$) of the doublet state. The first $\nu_{Ni-N(CS)}$ (cal. 230 cm$^{-1}$) is assigned at 223 cm$^{-1}$, which is overlapped with that of the quartet state. This doublet state appearing at higher temperatures ought to lie above the quartet state. At room temperature, the doublet state already had some population.

Figure S8 shows the SERS spectra from 77 to 623 K for [Ni$_3$(dpa)$_4$Cl$_2$]. In these spectra, the intensities of the 242 cm$^{-1}$ bands ($\nu_{Ni-Cl}$ of the doublet state) were weak and, thus, noticeable only at higher temperatures for the chloride complex. From the calculations, the Ni–Cl stretching modes lie at 245 and 229 cm$^{-1}$ for the doublet ($C_4$) and quartet states ($D_4$), respectively. In addition, according to the calculated results, the energy variation of the doublet and the quartet state is the same for both complexes with axial ligands Cl and NCS. The calculated energy gap of the doublet and quartet states is $\approx$ 22 kJ mol$^{-1}$, which is much greater than expected, based on the experimental observation that Raman bands appear for both doublet and quartet states at room temperature. Similar to B3LYP, B3LYP*-D3 might underestimate the energy of the high-spin state to some extent. Table 4 lists the experimental and calculated electronic transitions and assignments.

3. CONCLUSIONS

In Figure 9, the electron configurations and energy levels of the spin states for oxidized, neutral, and reduced Ni$_3$(dpa)$_3$X$_3$ are depicted. The theoretical DFT method B3LYP*-D3, including less exact exchange energy and van der Waals interaction of metal ions, yielded the geometries and vibrational structures of trinickel EMACs in agreement with the experimental data. These calculations provide adequate assignments of the vibrational and electronic spectra of various spin states. The molecular orbital models suggested in the present work and the DFT method B3LYP*-D3 may be applied to other EMACs containing first-row transition metals.$^{34}$ From analyzing the MOs, a complex exhibits a LMO type of bonding, yielding nearly independent metal-centered moieties, and most likely less metal–metal bonding in these complexes.

The ground state of Ni$_3$(dpa)$_3$X$_3$ is an antiferromagnetic (AF) singlet state corresponding to a LMO type of bonding. The quintet state, having a geometry similar to the ground state, was detected using Raman spectroscopy under a magnetic field and at high temperatures. When Ni$_3$(dpa)$_3$X$_3$ was oxidized, two complexes with [Ni$_3$]$^{7+}$ cores were identified—the doublet [Ni$_3$(dpa)$_3$]$^{3+}$ and the quartet [Ni$_3$(dpa)$_3$X]$^+$. According to the SERS and electrochemical measurements, complex [Ni$_3$(dpa)$_3$]$^{3+}$ has a doublet state as the ground state and [Ni$_3$(dpa)$_3$X]$^+$ as a quartet state. This quartet state has a LMO type of bonding, yielding long Ni–Ni and short Ni–Cl bond lengths. However, the doublet of [Ni$_3$(dpa)$_3$]$^{3+}$ has a DMO-type bonding with short Ni–Ni bond lengths, distinct from those of quartet [Ni$_3$(dpa)$_3$X]$^+$. For the reduced form [Ni$_3$(dpa)$_3$Cl$_2$]$^-$, the quartet state with LMO-type bonding is the ground state, but the doublet state lies close; hence, at room temperature, both spin states were detected by SERS measurements.

4. EXPERIMENTAL SECTION

4.1. Materials and SERS Sample Preparation. Complex Ni$_3$(dpa)$_3$X$_3$ was synthesized according to a previous method.$^7$
Gold(III) chloride trihydrate (HAuCl₄·3H₂O) was purchased from Alfa Aesar, and sodium citrate was obtained from Sigma-Aldrich. The SERS samples were prepared by dissolving Ni₃(dpa)₄X₂ powder with ethanol, and the solution was then mixed with AuNP solution, dripped on a quartz plate, and dried under vacuum. The AuNP solution was prepared by adding 0.5 mL of 0.029 M HAuCl₄ to 49.5 mL H₂O and then adding 0.1 g of sodium citrate, and it was heated to 343 K. The solution was stirred constantly until the color changed from yellow to red.

4.2. Temperature-Dependent Raman and SERS Measurements. All Raman spectra were recorded using a 632.8 nm He–Ne laser (Lasercom) as the excitation light, which passed through the laser line filter in a backscattering setup. The laser light was reflected by an edge filter (Semrock) and focused through an objective (10X, NA = 0.26) onto a sample cell (Linkam), the interior temperature of which was varied from 77 to 623 K. The scattered signal returned to the edge filter, passed through two BraggGrate notch filters, which blocked the Rayleigh scattering, and then reached a monochromator (length, 0.5 m; grating 600 grooves/mm, 1800 grooves/mm for high resolution), after which it was detected by a liquid nitrogen-cooled charge-coupled device (CCD). The signal was accumulated for 2–3 min for each scan and was averaged over 15 scans. We used single crystals in the Raman measurements, and a thin permanent magnet of 2400 G was inserted under the sample cell when the magnetic field was applied. The spectral resolutions were 2 and 0.5 cm⁻¹ for the regular and high-resolution measurements, respectively.

5. COMPUTATIONAL DETAILS

All geometry optimizations and spectral calculations were performed using the Gaussian 16 package. The modified hybrid functional B3LYP*-D3 was employed for most molecules unless otherwise specified. The basis sets were 6-31G(d) for C and H, 6-311G(d) for N and the axial ligands, and def2-TZVP for Ni atoms for all B3LYP* calculations. For comparison, we also used the GGA functional BP86 with software ORCA 4.1.1, which provided a better density fitting method, RIJCOX, for Coulomb integrals and exchange integrals to speed up the calculations. The basis sets used in this method were def2-SVP for C and H, def2-TZVP for N and the axial ligands, and def2-TZVPP for Ni, and the auxiliary basis set was def2/J for the density fitting method. Time-dependent DFT (TD-DFT) was used in calculating the vertical transitions to excited states, and some specific transitions were analyzed using Multiwfn 3.6 software, which provided the hole–electron distribution of a specific electronic transition and the interference charge transfer (IFCT) to yield the variation of the electron population among molecular moieties. The X-ray crystal structure of the complex Ni₃(dpa)₄Cl₂ from the Cambridge Structural Database (CSD) was used as the initial input geometry in the structural optimization. The antiferromagnetic (AF) states of Ni₃(dpa)₄Cl₂ were obtained by the broken-symmetry (BS) method; the molecule was divided into fragments, which set their own spins in the calculations.

The dispersion correction D3 method reported by Grimme et al. was used here to include the weak interaction between atoms in the B3LYP* method. The Becke and Johnson (BJ) damping function was selected, rather than zero-damping. This semicalssical correction D3 gave rise to minor corrections on geometries; thus, the vibrational structures were accord-ingly slightly varied but had virtually no influence on the absorption spectra.

The magnetic properties of the molecules were simply defined by Heisenberg–Dirac–van Vleck (HDVV) approximation

\[ \hat{H} = -2 \sum_{a>b} J_{ab} \hat{S}_a \cdot \hat{S}_b \]  

where \( J_{ab} \) is the effective exchange constant between the sites \( a \) and \( b \) with spin operators \( \hat{S}_a \) and \( \hat{S}_b \) respectively. Broken-symmetry states were obtained from mixing the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO) and resulted in spin contamination of the high-spin states for low-spin states. Thus, the magnitude of the exchange constant \( J_{ab} \) was unable to reproduce the results of the magnetic susceptibility measurements. Yamaguchi et al. proposed a spin-projection procedure to estimate the exchange constant \( J_{ab} \) from the broken-symmetry method. The exchange constant was defined as follows

\[ J_{ab} = \frac{E^{LS}_{BS} - E^{HS}}{\langle S^2 \rangle^{HS} - \langle S^2 \rangle^{LS}} \]  

where \( \langle S^2 \rangle \) is the eigenvalue of the total spin operator squared for the high-spin and low-spin states, which belonged to the antiferromagnetic singlet state in this case. The approximate \( J_{ab} \) in eq 2 is equal to the results calculated by spin-projected wavefunctions. Basically, the spin contamination of the high-spin state could be ignored, and the spin-projection total energy of the antiferromagnetic singlet state (\( E_{APBS} \)) was approximately obtained as

\[ E_{APBS}^{LS} = \alpha E_{BS}^{LS} - \beta E_{BS}^{HS} \]  

where

\[ \alpha = \frac{\langle S^2 \rangle^{HS} - \langle S^2 \rangle^{exact}^{HS}}{\langle S^2 \rangle^{HS} - \langle S^2 \rangle^{BS}^{HS}} \]  

and

\[ \beta = \frac{\langle S^2 \rangle^{BS}^{LS} - \langle S^2 \rangle^{exact}^{HS}}{\langle S^2 \rangle^{HS} - \langle S^2 \rangle^{BS}^{HS}} \]  

Through the approximate spin-projection (AP) method, the spin contamination was eliminated and the energy of a broken-symmetry state was corrected.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01844.

Electronic transitions of complexes, analyzed hole–electron distributions of various transitions, Raman curves measured at temperatures of 77–623 K (Figure S1); temperature-dependent Raman curves of Ni₃(dpa)₄Cl₂ from 77 to 623 K (Figure S2); list of contributions of components and oscillator strength of vertical transitions of Ni₃(dpa)₄Cl₂ analyzed using the IFC method (Table S1) (PDF)

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Notes
The authors declare no competing financial interest.

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