Effect of axial anthracene ligands on the luminescence of trinickel molecular wires

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Dedicated to Prof. F.A. Cotton, deceased February 20, 2007

Abstract

Two nickel compounds having extended metal atom chains (EMACs) with the $Ni_3(dpa)_4L_2$ core, where dpa is the anion of 2,2′-dipyridylamine and L represents an anthracene derivative, have been synthesized in good yield and excellent purity by reaction of $Ni_3(dpa)_4Cl_2$ and the respective anthracene derivatives. For the compound $Ni_3(dpa)_4(AnCC)_2$ (**1**) AnCC is the anion of 9-ethynylanthracene and for $Ni_3(dpa)_4(AnCOO)_2$ (**2**) AnCOO is anthracene-9-carboxylate. The two compounds have been characterized by X-ray crystallography and other techniques. The cyclovoltammograms (CVs) of **1** and **2** display reversible redox processes at $E_{1/2} = 0.911$ V and 1.020 V, respectively (vs. Ag/AgCl). The magnetic data suggest that the terminal Ni atoms are in a high spin state while the central Ni atom is diamagnetic, in agreement with other trinickel molecular wires. Although compound **1** is strongly luminescent, and represents the first such example in an EMAC, **2** does not display luminescence. The strong emission in **1** is related to donor–acceptor interactions between the Ni···Ni···Ni wire, the triply bonded C≡C linking unit, and the conjugated aromatic anthracene derivative, a process that is unavailable for **2** because the carboxylate group is almost perpendicular to the anthracene moiety.
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1. Introduction

Great efforts have been devoted recently with the aim of preparing molecules having multimetal units that lead to special physical properties, such as conductivity, magnetism, and optical activity [1]. For example, a variety of complexes containing multiple Mn atoms have been designed as single-molecule magnets, which are of potential importance in data storage [2]. Also a novel metallamacrocyclic gold(I) thiolate cluster complex having weak intermolecular aurophilic Au–Au interactions has been suggested for the design of electronic and sensor devices [2].

Even though the *molecular wire* concept was introduced long ago, interest on such species continues because of their potential applications [3]. We have been especially interested in *extended metal atom chains* (EMACs). The field of EMACs can be traced back to 1968 when a compound having the formula $Ni_3(dpa)_4Cl_2$ was reported [4] but growth did not initiate until the correct structure was determined in 1991 [5]. We and Peng's group in Taipei have utilized linear polypyridylamido ligands to synthesize a variety of EMACs [6], which include metal atom chains having Cr [7], Co [8], Ni [9], Cu [10], Ru [11] and Rh [12] with or without metal–metal bonds between metal atoms. The number of metal atoms in these EMACs vary from three to nine [6,13], and the length ranges from about ∼5 Å for a three metal atom chain to ∼18 Å for the nine metal atom chain. Because the metal units may provide a

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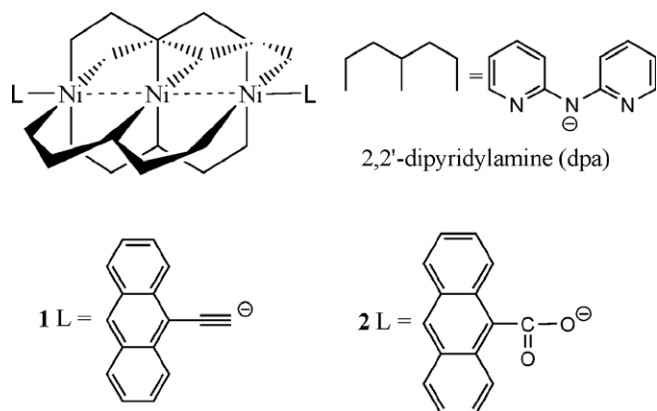
Scheme 1.

path for electrons, there is potential for conducting properties and use as molecular wires in nanoscale electronic devices. A well-studied example is $Ni_3(dpa)_4Cl_2$ (dpa = 2,2'-dipyridylamide), which shows single-electron tunneling behavior and the energies of the vibrational states are dependent on the redox state of the molecules [14]. Exchange of axial ligands in $Ni_3(dpa)_4Cl_2$, such in the formation of $Ni_3(dpa)_4(CN)_2$, $Ni_3(dpa)_4(NCNCN)_2$, and $Ni_3(dpa)_4(C{\equiv}CPh)_2$ modify the electrochemical properties of the Ni_3^{6+} species [15].
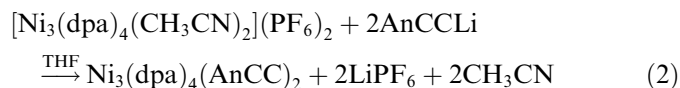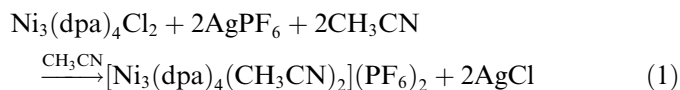
Because anthracene units are known to induce luminescence in certain species and have been used extensively for the syntheses of optical materials [16], we decided to study the effect of such electron-rich anthracene units in EMACs. It was found that depending of the chemical group used to link the EMAC to the anthracene derivative, e.g., acetylide or carboxylate, the luminescence can be tuned. Here we report the preparation of $Ni_3(dpa)_4(AnCC)_2$ (1) and $Ni_3(dpa)_4(AnCOO)_2$ (2) where AnCC is the anion of 9-ethynylanthracene and AnCOO represents the anion of anthracene-9-carboxylic acid (Scheme 1). Both of compounds have been characterized by X-ray crystallography and their electrochemistry and magnetism are compared to those of other EMACs.

2. Results and discussion

2.1. Syntheses

Early work showed that direct reaction of $Ni_3(dpa)_4Cl_2$ with anionic ligands, such as phenylacetylene was difficult and often led to partial substitution of the axial ligands [15]. However, the Cl groups can be replaced by mixing $Ni_3(dpa)_4Cl_2$ and AgPF$_6$ in acetonitrile, in a reaction that produces $[Ni_3(dpa)_4(CH_3CN)_2](PF_6)_2$, as shown in Eq. (1). Because the axial CH_3CN ligands in this compound are labile, they can be easily displaced by anionic ligands to form other $Ni_3(dpa)_4L_2$ compounds in good yield and purity [17]. Here we utilize large conjugated 9-ethynylanthracene ligands to replace the acetonitrile molecules.

When an acetonitrile solution of $[Ni_3(dpa)_4(CH_3CN)_2](PF_6)_2$ was treated with excess lithium 9-ethynylanthracene in THF (see Eq. (2)), the neutral compound $Ni_3(dpa)_4(AnCC)_2$ (1) was easily isolated because it is insoluble in polar solvents.

$$Ni_3(dpa)_4Cl_2 + 2AgPF_6 + 2CH_3CN$$
$$\xrightarrow{CH_3CN} [Ni_3(dpa)_4(CH_3CN)_2](PF_6)_2 + 2AgCl \quad (1)$$

$$[Ni_3(dpa)_4(CH_3CN)_2](PF_6)_2 + 2AnCCLi$$
$$\xrightarrow{THF} Ni_3(dpa)_4(AnCC)_2 + 2LiPF_6 + 2CH_3CN \quad (2)$$

Compound 2, $Ni_3(dpa)_4(AnCOO)_2$, was synthesized similarly to 1 but using a slightly modified procedure, as shown in Eq. (3). A solution of the precursor $Ni_3(dpa)_4Cl_2$ in methanol was reacted with TlPF$_6$. Removal of the axial Cl ligands by precipitation of TlCl followed by *in situ* addition of AnCOONa gave analytically pure $Ni_3(dpa)_4(AnCOO)_2$.

$$[Ni_3(dpa)_4Cl_2 + 2TlPF_6 + 2AnCOONa$$
$$\xrightarrow{CH_3OH} Ni_3(dpa)_4(AnCOO)_2 + 2TlCl + 2NaPF_6 \quad (3)$$
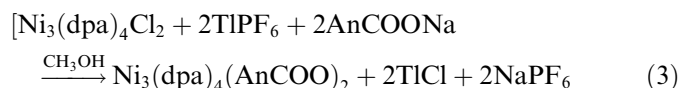
2.2. Structural results

Structures of 1 and 2, showing the typical helical arrangement of the $Ni_3(dpa)_4^{2+}$ core, are provided in Fig. 1 [6,18]. Compound 1 crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$. The crystallographic independent $Ni{\cdots}Ni$ distances of 2.4781(9) and 2.4804(9) Å are statistically equivalent. These distances are comparable to those in analogues with axial Ni–C bonds such as $Ni_3(dpa)_4(CN)_2$ and $Ni_3(dpa)_4(CCPh)_2$ (2.4523(3) and 2.479[3] Å, respectively) [15]. These $Ni{\cdots}Ni$ distances are significantly longer than the corresponding distances in $Ni_3(dpa)_4Cl_2$ (2.430[9] Å) due to the strong basicity of the $AnCC^-$ anion. In this compound, the two $C{\equiv}C$ triple bond lengths are 1.221(7) and 1.211(6) Å, and the $Ni{-}C{\equiv}C$ units are essentially linear with angles of 175.7(5)° and 167.6(4)°. The anthracene rings are planar. Additional bond distances and angles are in Table 1.

Compound 2 crystallizes in the tetragonal space group $P4_2/n$ with $Z = 8$. Because the $AnCOO^-$ anion is a weak base, the $Ni{\cdots}Ni$ separations of 2.4249(10) and 2.4223(10) Å are comparable with those in $Ni_3(dpa)_4Cl_2$. However, these separations are longer than those in analogous compounds with neutral donor ligands, e.g., acetonitrile in $[Ni_3(dpa)_4(CH_3CN)_2](PF_6)_2$ (2.374[2] Å) [6]. Similar to other Ni_3^{6+} compounds, the outer Ni–N distances for both 1 and 2 are about 0.11 Å longer than the corresponding distances for the inner Ni atom, since the outer Ni atoms are five-coordinate and high spin while the central Ni unit is square planar and expected to be diamagnetic. It should be noted that in 2 the anthracene moieties are essentially perpendicular to the carboxylate group (Fig. 1).
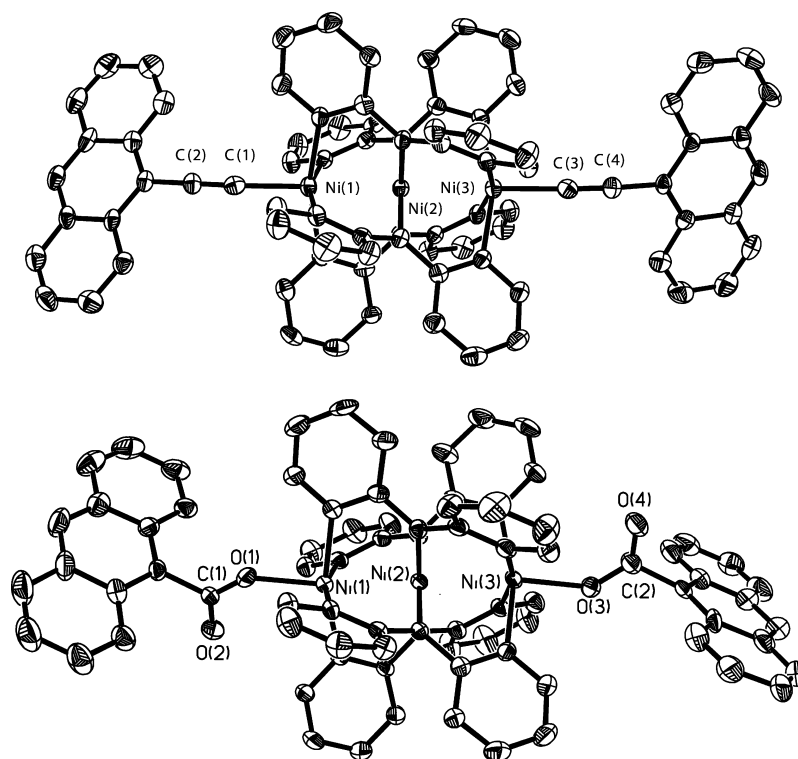
Fig. 1. Molecular structures of **1** (top) and **2** (bottom) drawn with ellipsoids at the 40% probability level. All hydrogen atoms have been omitted for clarity. Note that for **2** the carboxylate groups are almost perpendicular to the anthracenyl moieties.

Table 1
Selected bond distances (Å) and angles (°) for **1** and **2**

	1 · 3C$_7$H$_8$	**2** · 0.75C$_6$H$_6$
Ni(1)···Ni(2)	2.4781(9)	2.4248(9)
Ni(2)···Ni(3)	2.4804(9)	2.4220(9)
Ni$_{outer}$–N$_{(av)}$	2.104[4]	2.098[7]
Ni$_{inner}$–N$_{(av)}$	1.893[5]	1.888[6]
Ni–X$^a_{axial}$ (av)	1.997[7]	2.007[6]
Ni(1)···Ni(2)···Ni(3)	178.77(4)	179.62(4)
C(1)–Ni(1)···Ni(2)	176.9(1)	
O(1)–Ni(1)···Ni(2)		171.5(1)
C(3)–Ni(3)···Ni(2)	178.9(2)	
O(3)–Ni(3)···Ni(2)		170.4(1)

^{a} X = C for **1**, and X = O for **2**.

2.3. Luminescence studies

Although many trimetal EMACs have been synthesized, luminescence properties have not been examined. Here we report our first efforts in this field by studying the effect of axial binding on the molecular wires. It is well-known that conjugated functional organic molecules are useful for the study of electron transport at the molecular scale and that the use of fused-ring systems is a powerful and practical approach [19]. Among the fused aromatic systems, anthracene units impart interesting luminescence properties to various materials [20].

We have noticed that solutions of Ni$_3$(dpa)$_4$Cl$_2$ in CH$_2$Cl$_2$ did not luminesce at room temperature after irradiation with light having an excitation wavelength of

370 nm. However, dichloromethane solutions of **1** display greenish-blue luminescence at room temperature with emission bands having λ_{max} at 410, 435, 460 and 490 nm when excited using light with a wavelength of 382 nm. As shown in Fig. 2, the emission maxima are shifted from that in the ligand precursor AnCCH. This is not unusual on itself as luminescence has been observed in other systems incorporating anthracene derivatives, such as in aryleneethylnyl-
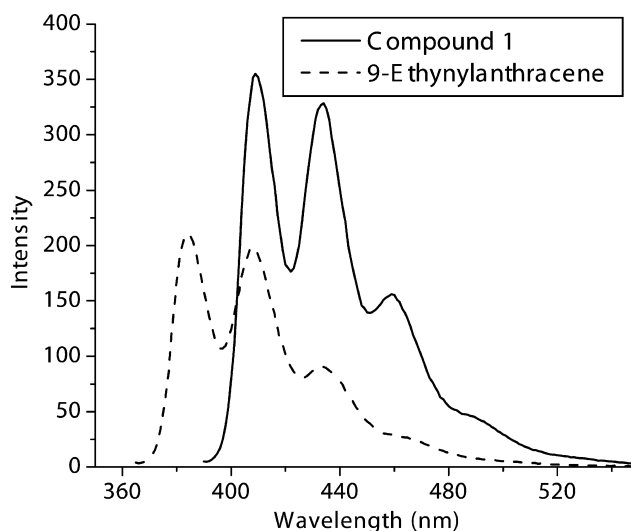

Fig. 2. The emission spectra for **1** (solid line) and its ligand precursor, 9-ethynylanthracene = AnCCH (dashed line) in CH$_2$Cl$_2$ solution at room temperature using an excitation wavelength of 382 nm.

enesilylene, which has extensive conjugation along the backbone, through–Si atoms [21], and in species having platinum dimers and polymers which have strong donor–acceptor interactions between the Pt(II) centers and conjugated ligands along the rigid backbone [22].

What is remarkable is that when the axial ligands were AnCOO$^-$ anions as in **2**, no significant luminescence was observed at room temperature upon irradiation of CH$_2$Cl$_2$ solutions using a source having a wavelength of 306 nm even though the ligand precursor (AnCOOH) is luminescent both in solution [23] and in the solid state where it dimerizes forming an essentially planar arrangement [24]. We believe that the quenching of the luminescence in **2** is due to the conformation of the axial AnCOO$^-$ ligands in which the carboxylate units are almost perpendicular to the anthracenyl groups. The dramatic difference in luminescence for species that contain anthracene derivatives in axial positions suggest that the mechanism may be affected by the degree of conjugation of the ligands with the molecular wire. In **1**, the two anthracene units and trinickel unit are linked by a unit containing a C≡C triple bond. In this arrangement, the anthracenyl and acetylide units are in a plane and therefore, the π electrons are delocalized, a pathway that is not available in **2**. It is perhaps relevant that because of the ability to delocalize electrons bisacetylide derivatives having anthracenyl groups have been used to probe electron exchange between two single metal units [25] or two dimetal units [26].

Another interesting observation is that the luminescence in dichloromethane solutions significantly decrease as the concentration of **1** increases in the range of 1×10^{-6}–1×10^{-4} M (Fig. 3). At a concentration of 1×10^{-3} M in CH$_2$Cl$_2$, the luminescence is completely quenched, which suggests that the degree of aggregation must be important. Furthermore, no luminescence was observed in the solid state neither at room temperature nor at 77 K. The crystal packing pattern, shown in Fig. 4, suggests a reason for this behavior as there are interactions between molecules that allow a pathway to dissipate energy excitations. The shortest distance between two neighboring molecules is only 2.716 Å. This is consistent with observations that quenching often depends on the molecular environment [27]. It has been noted that in general aggregation in the solid state causes undesirable red shifts in the emission spectra and/or emission quenching [28]. It is also known that interstitial solvent molecules can also quench emissions [29]. Because there are toluene molecules between layers in crystals of **1** having distances as short as 2.799 Å this may also contribute to the decrease in luminescence. Indeed solutions of **1** in toluene with concentrations ranging from 1×10^{-6} to 1×10^{-4} M are inactive and show no luminescence.

2.4. Electrochemistry

In previous reports [6], it has been shown that the oxidation potentials for the one-electron oxidation of Ni$_3$(dpa)$_4$L$_2$ compounds range from 0.767 to 1.205 V (in CH$_2$Cl$_2$ solution, vs. Ag/AgCl). The variations are due effect on the HOMO of trinickel compounds by the axial ligands which cause a significant change in oxidation potentials. The CVs of **1** and **2** in CH$_2$Cl$_2$ solution using Bu$_4^n$NPF$_6$ as electrolyte are shown in Fig. 5. The oxidation potential of 0.911 V for **1** is close to that of 0.908 V for Ni$_3$(dpa)$_4$Cl$_2$, while compound **2** has higher oxidation potential, 1.020 V. In both compounds the redox processes are reversible.
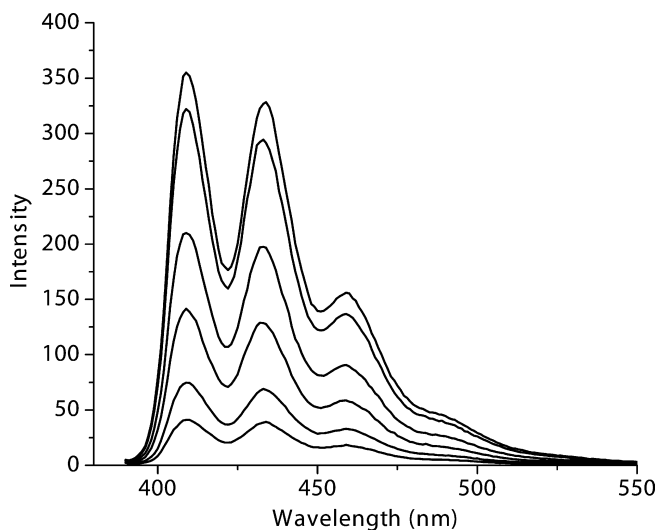
Fig. 3. Variation of the luminescence in solutions of **1** as the concentration in CH$_2$Cl$_2$ increases from 1×10^{-6} (top trace) to 1×10^{-4} M (bottom trace).
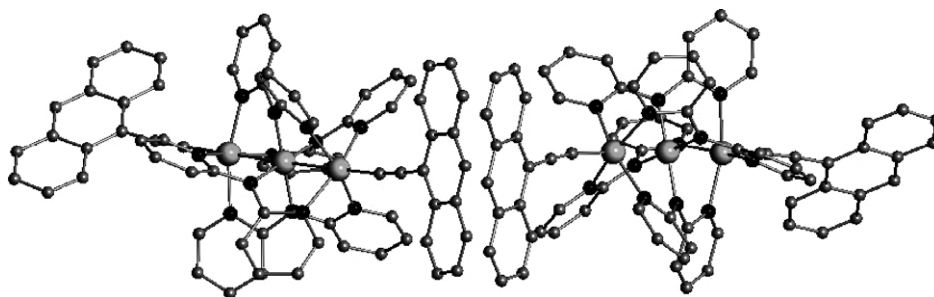
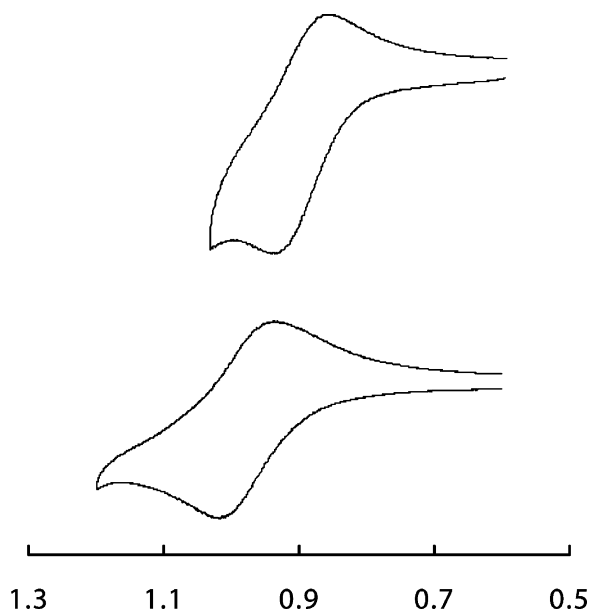Fig. 4. Crystal packing pattern for compound **1**.

Fig. 5. Cyclic voltammograms of **1** and **2** in CH_2Cl_2 solution. Potentials are referenced to the Ag/AgCl electrode.

2.5. Magnetic susceptibility

The variable temperature magnetic data for **1** and **2** are shown in Fig. 6. The shape of the curves resembles those in the analogous chloro complex and other Ni_3^{6+} EMACs [15]. In these complexes, the inner Ni atom is square planar and diamagnetic while the outer Ni atoms are high spin with two unpaired electrons each, and the unpaired electrons couple antiferromagnetically through the inner Ni atom (Scheme 2). At 300 K, the χT values are less than 2.00 emu K/mol (1.26 for **1** and 1.10 for **2**) for two independent $S = 1$ centers, which means that the spins are only partially randomized. The lower χT value for **2** suggests that the magnetic coupling is stronger than that for **1**. The χT values for both compounds decrease as the temper-
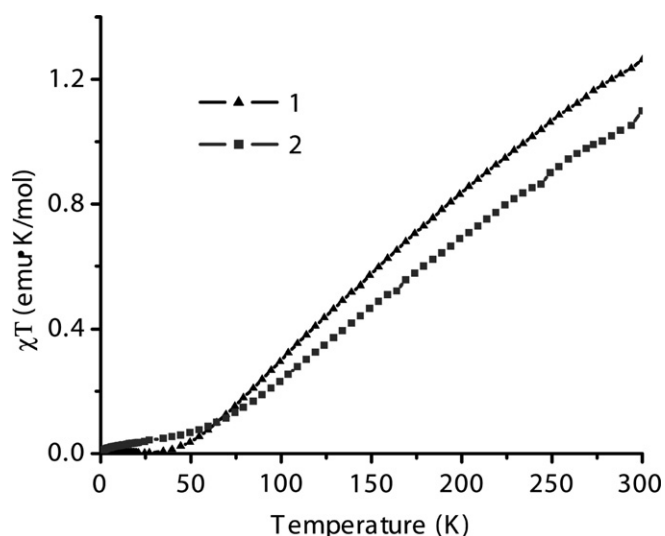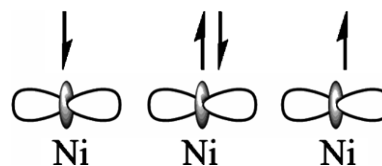

Fig. 6. Magnetic susceptibility data for **1** and **2** in the range of 2–300 K.

Scheme 2.

ature decreases, and χT values are essentially zero below 40 K, indicating a spin state of $S = 0$ is the ground state. The difference in patterns for the χT vs. T indicates that the values of J depend on the nature of the axial ligands. These magnetic data has been modeled using the spin Hamiltonian $H = -JS_1 \cdot S_3$, and Eq. (4) was used to fit the data for **1** and **2**:

$$\chi = \frac{2Ng^2\beta^2(e^{J/kT} + 5e^{3J/kT})}{kT(1 + 3e^{J/kT} + 5e^{3J/kT})} \qquad (4)$$

where N is Avogadro's number, g is the Landé factor, β is the electron Bohr magneton, k is the Boltzmann constant, J is the exchange parameter, and T is the absolute temperature.

Even though both are simple exchange-coupling trinickel systems, the degree of antiferromagnetic coupling is different. Values of $g = 2.21$, $J = -228$ cm^{-1} for **1** and $g = 2.13$, $J = -260$ cm^{-1} for **2** gave satisfactory least-squares fits. The values of g are similar to those of other Ni_3^{6+} EMACs, but the values of J are more negative than those of the chloro analogue (-218.2 cm^{-1}) [6]. Previous studies on a series of trinickel compounds have shown that the exchange parameter J is related to the Ni$\cdots$Ni distances [15]. Longer Ni$\cdots$Ni distances lead to weak antiferromagnetic coupling. The more negative J value for **2** is consistent with the structural data since the Ni$\cdots$Ni distances for compound **2** are about 0.05 Å shorter than for **1**.

3. Conclusions

Two trinickel EMACs, **1** and **2**, have been made with anthracene derivatives in axial positions. Both have similar overall structures but small variations in the axial ligands influence the Ni$\cdots$Ni distances, magnetic susceptibilities, and optical properties. The Ni$\cdots$Ni distance of **1** is slightly longer than that of **2**, which lead to slightly stronger antiferromagnetic coupling in **2**. More importantly, compounds **1** and **2** show different luminescence behavior due to differences in conformation of the anthracene derivatives. The C≡C triple bonds in the axial ligands in **1** facilitate electron delocalization between the anthracene units and the trimetal center and result in luminescence emission.

4. Experimental

4.1. Materials and methods

All reactions and manipulations were carried out under dry nitrogen using standard Schlenk techniques. All

solvents were either distilled over appropriate drying agents in a nitrogen atmosphere or purified using a Glass Contour solvent system. All chemicals were purchased from Aldrich and 2,2′-dipyridylamide was sublimed prior to use. Anhydrous nickel chloride, silver(I) hexafluorophosphate and thallium(I) hexafluorophosphate were dried overnight under vacuum at 70 °C prior to use, and other commercial chemicals were used as received. Methyllithium (1.6 M in ether) and sodium methoxide (0.5 M in methanol) were kept in a refrigerator prior to use.

The ligand 9-ethynylanthracene (AnC≡CH) was prepared from 9-bromoanthracene using a previously described two-step process [30]. The nickel-containing starting material $Ni_3(dpa)_4Cl_2$ was synthesized according to a previously reported method [31]. $[Ni_3(dpa)_4(CH_3CN)_2](PF_6)_2$ was synthesized in acetonitrile by reaction of $Ni_3(dpa)_4Cl_2$ with 2 equiv. of $AgPF_6$ [32].

4.2. Analytical and physical measurements

Elemental analyses were performed by Robertson Microlit Laboratories, Madison, NJ. Mass spectrometric data were recorded at the Laboratory for Biological Mass Spectrometry at Texas A&M University. ^1H NMR spectra were obtained on a Mercury 300 NMR spectrometer with chemical shifts referenced to DMSO ($\delta = 2.49$ ppm). UV–vis spectra were measured on a Shimadzu UV-2501PC spectrophotometer in dichloromethane solution. The cyclic voltammograms (CVs) were taken on a CH Instruments electrochemical analyzer with $Bu_4^nNPF_6$ (0.1 M in CH_2Cl_2) electrolyte, Pt working and auxiliary electrodes, an Ag/AgCl reference electrode, and a scan rate (for CVs) of 100 mV/s. Variable temperature magnetic susceptibility measurements were performed on a Quantum Design SQUID (Superconducting Quantum Interference Device) magnetometer MPMS-XL from 2 to 300 K. Luminescence spectra were recorded at ambient temperature on a Varian Cary Eclipse Fluorescence Spectrophotometer using excitation wavelengths of 382 nm and 306 nm for compounds **1** and **2**, respectively.

4.3. Preparation of Ni₃(dpa)₄(AnCC)₂ (1)

9-Ethynylanthracene (AnC≡CH, 0.13 g, 0.64 mmol) was dissolved in 5 mL of THF and the solution cooled to 0 °C using an ice water bath. A solution of MeLi (1.6 M in ether, 0.40 mL) was added slowly. The mixture was allowed to reach room temperature giving a pale yellow suspension, which was transferred to a flask containing $[Ni_3(dpa)_4(CH_3CN)_2](PF_6)_2$ (0.18 g, 0.13 mmol) in 15 mL of acetonitrile. After stirring the mixture for 3 h, a brown-purple precipitate formed. The supernatant solution was decanted and the remaining solid was washed with ether (2 × 15 mL), dried under vacuum for 2 h, and then toluene (10 mL) was added. The brown-purple mixture was filtered, and the filtrate was layered with isomeric hexanes (30 mL). Deep brown-purple crystals formed within a week. Yield:

97 mg, 52%. Anal. Calc. for $C_{72}H_{50}N_{12}Ni_3$ (**1**): C, 68.06; H, 4.00; N, 13.35. Found: C, 67.62; H, 3.58; N, 13.05%. Mass spectrum, ESI$^+$ (m/z): 629.54 $[Ni_3(dpa)_4(AnCC)_2]^{2+}$, 538.18 $[Ni_3(dpa)_4(AnCC)(H_2O)]^{2+}$. UV–vis in CH_2Cl_2, λ_{max} (nm) (ε, M^{-1} cm^{-1}): 505 (3000), 600 (1000).

4.4. Preparation of Ni₃(dpa)₄(AnCOO)₂ (2)

To a flask containing a sample of crystalline $Ni_3(dpa)_4$-Cl_2 (93 mg, 0.10 mmol) and $TlPF_6$ (87 mg, 0.25 mmol) was added 15 mL of methanol. The purple solution was stirred for 3 h, whereupon a white precipitate of TlCl was observed. The mixture was filtered through a frit packed with Celite. A methanol solution (10 mL) of AnCOONa, prepared in situ by reaction of $NaOCH_3$ (0.5 M in methanol, 0.50 mL) and anthracene-9-carboxylic acid (AnCOOH, 56 mg, 0.25 mmol), was then transferred by cannula to the filtrate. After stirring the resulting mixture for 5 h at room temperature, the solvent was removed under vacuum and the residue was washed with ether (2 × 15 mL), dried under vacuum for 2 h, and extracted with 10 mL of benzene. After filtration, the red-purple filtrate was layered with hexanes (40 mL). Large block-shaped red-purple crystals formed over the course of a week. Yield: 96 mg, 74%. Anal. Calc. for $C_{70}H_{54}N_{12}Ni_3O_6$ (**2** · 2 H_2O): C, 62.96; H, 4.01; N, 12.58. Found: C, 62.71; H, 3.57; N, 12.96%. Mass spectrum, ESI$^+$ (m/z): 428.05 $[Ni_3(dpa)_4]^{2+}$, 1077.16 $[Ni_3(dpa)_4(AnCOO)]^+$. UV–vis in CH_2Cl_2, λ_{max} (nm) (ε, M^{-1} cm^{-1}): 520 (3000), 620 (500).

4.5. X-ray structural determinations

For each compound a suitable crystal was mounted at the end of a quartz fiber with the aid of a small amount

Table 2
X-ray crystallographic data

Compound	$1 \cdot 3C_7H_8$	$2 \cdot 0.75C_6H_6$
Formula	$C_{86}H_{59}N_{12}Ni_3$	$C_{74.5}H_{54.5}N_{12}Ni_3O_4$
MW	1436.58	1357.93
Crystal system	Monoclinic	Tetragonal
Space group	$P2_1/c$	$P4_2/n$
a (Å)	24.696(3)	32.300(5)
b (Å)	11.396(2)	32.300(5)
c (Å)	26.708(4)	13.094(3)
α (°)	90	90
β (°)	108.602(3)	90
γ (°)	90	90
V (Å³)	7124(2)	13661(4)
Z	4	8
T (K)	213	213
λ (Å)	0.71073	0.71073
d_{calcd} (g cm⁻³)	1.339	1.264
Number of reflections	31096	70905
Number of parameters	879	914
Number of R_{int}	10024 (0.0598)	12037 (0.0738)
R_1^a, wR_2^b ($I > 2\sigma I$)	0.0472, 0.0853	0.0569, 0.1452
R_1^a, wR_2^b (all data)	0.0918, 0.1042	0.1020, 0.1766

[a] $R_1 = \sum ||F_o| - |F_c||/\sum |F_o|$.
[b] $wR_2 = [\sum [w(F_o^2 - F_c^2)^2]/\sum [w(F_o^2)^2]]^{1/2}$.

of stopcock grease and was placed on a goniometer head. X-ray diffraction data for **1** · 3C$_7$H$_8$ and **2** · 0.75C$_6$H$_6$ were collected at 213 K on a Bruker SMART 1000 CCD area detector system [33]. Data reduction and integration were performed using the software SAINTPLUS [34]. Absorption corrections were applied using the program SADABS [35]. All the structures were solved by direct methods and refined using the SHELXL-97 program [36]. Subsequent cycles of least-squares refinement followed by difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. In all structures, hydrogen atoms were added at calculated positions based on a riding model. The interstitial molecules in **1** · 3C$_7$H$_8$ and the anthracene unit in **2** · 0.75C$_6$H$_6$ were disordered. Non-hydrogen atoms, except some disordered atoms, were refined with anisotropic displacement parameters. Crystallographic data for **1** · 3C$_7$H$_8$ and **2** · 0.75C$_6$H$_6$ are given in Table 2.

5. Supplementary material

CCDC 641675 and 641676 contain the supplementary crystallographic data for **1** · 3C$_7$H$_8$ and **2** · 0.75C$_6$H$_6$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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