Manipulation of electronic structure *via* supporting ligands: a charge disproportionate model within the linear metal framework of asymmetric nickel string [Ni₇(phdptrany)₄Cl](PF₆)[†]

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This paper describes the synthesis and physical properties of an uniquely asymmetric heptanickel string complex exhibiting a charge disproportionate model along the linear nickel framework.

1D transition-metal complexes are of considerable significance for their potential applications as molecular wires, since these complexes may be envisaged as the macroscopic wires in miniature at the atomic scale.¹ In order to design new molecular wires, we have reported that novel metal string complexes can be synthesized by using naphthyridyl-modulated ligands.² The modulation of the supporting ligands results in a remarkable influence on the physical properties of the oligonickel string complexes because of the formation of mixedvalence (MV) dinickel units $[Ni_2(napy)_4]^{3+}$ (napy = naphthyridyl group) within the linear metal framework. It is known that the mixed-valency plays an important role in the development of novel electronic materials.³ This MV $[Ni_2(napy)_4]^{3+}$ unit has been shown to exhibit a great electron mobility and can significantly enhance the conductance of metal string complexes.2a

In addition to above advances, another breakthrough in this field is the development of asymmetric ligands. By utilizing these ligands, the asymmetric electronic structures of metal frameworks, or the arrangement of hetero-metal ions of metal string complexes can be controlled.^{2b,c} Promoted by these recent studies, we designed a new asymmetric ligand H₃phdptrany (2-(phenyldipyridyltriamino)-1,8-naphthyridine, Scheme 1). The deprotonated counterpart phdptrany³⁻ shows two different coordinated abilities at both ends, since the naphthyridyl terminal is neutral and the phenylamido part is anionic. This new ligand can then be used to generate the related novel metal string complex. Herein, we report the synthesis and physical properties of the asymmetric heptanickel string complex, [Ni₇(phdptrany)₄Cl](PF₆) (1), which displays



Scheme 1

an intriguing charge disproportionate model controlled by the supporting ligand phdptrany^{3–}.

The overall synthetic routes to the H₃phdptrany ligand, and then to complex **1**, are summarized in Scheme S1 (see ESI†). The H₃phdptrany ligand was prepared by the reaction of aniline and 2-(bromodipyridyl-diamino)-1,8-naphthyridine with a palladium catalyst. Treatment of H₃phdptrany with NiCl₂ in the presence of ^{*t*}BuOK, followed by excess of KPF₆, generated compound **1**.

The crystal structure of **1** is depicted in Fig. 1.§ The linear heptanickel framework is helically wrapped by four phdptrany^{3–} ligands, which exhibits approximate C_4 symmetry. The Ni(1)–Ni(2), Ni(1)–N and Ni(2)–N distances are 2.327(1) Å, 2.145(6) Å and 2.024(6) Å, respectively, in accordance with the typical structural characteristics for the one-electron reduced S = 3/2 MV [Ni₂(napy)₄]³⁺ unit.² Interestingly, the Ni(5)–Ni(6) and N(6)–Ni(7) bond lengths of **1** are 2.253(1) and



Fig. 1 ORTEP view of the molecular structure of the $[Ni_7(phdptrany)_4-Cl](PF_6)$ (1, 30% probability). Selected bond distances (averaged): Ni(1)–Cl 2.405(2), Ni(1)–Ni(2) 2.327(1), Ni(2)–Ni(3) 2.314(1), Ni(3)–Ni(4) 2.287(1), Ni(4)–Ni(5) 2.255(1), Ni(5)–Ni(6) 2.253(1), Ni(6)–Ni(7) 2.305(1), Ni(1)–N 2.145(6), Ni(2)–N 2.024(6), Ni(3)–N 1.902(6), Ni(4)–N 1.909(6), Ni(5)–N 1.889(6), Ni(6)–N 1.912(6), Ni(7)–N 1.923(6) Å.

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Fig. 2 Near-IR spectrum of 1 CH₂Cl₂. Concentration: 2×10^{-5} M.

2.305(1) Å, respectively, shorter by ~0.05 Å in comparison with those of the reported asymmetrical hexanickel analogue (Ni(4)–Ni(5) and N(5)–Ni(6) bond distances in (4,0)-[Ni₆-(napany)₄Cl](BF₄)₂, napany²⁻ = (2-naphthyridylamido-7phenylamido-1,8-naphthyridine).^{2b}

The shortening of these Ni–Ni bonds close to the phenylamido groups of **1** suggests that the formation of the delocalized metal–metal bonding within the Ni(5)–Ni(6)–Ni(7) fragment due to the incomplete population of the σ^* orbital. This observation is reminiscent of the one-electron oxidized pentanickel complex.⁴ The structural features of **1**, therefore, suggest an unprecedented internal charge disproportionate mechanism along the metal framework: the nickel ion coordinated to the neutral naphthyridyl groups undergoes one-electron reduction, while those coordinated close to the anionic phenylamido groups undergo one-electron oxidation.

The near-IR spectrum of **1** reveals two broad absorptions at 1200 ($\varepsilon = 6890$) and 1700 nm ($\varepsilon = 2890$, Fig. 2). These two peaks can be tentatively assigned to intervalence charge transfer (IVCT) bands, which suggest the existance of mixed-valence units within the metal framework.^{2a}

The temperature-dependent magnetic susceptibility of **1** was measured in the range 4–300 K (Fig. 3). The $\chi_m T$ value at 300 K is 2.10 cm³ Kmol⁻¹, which is in agreement with the theoretical value for two independent S = 3/2 and S = 1/2 magnetic centers (2.25 cm³ Kmol⁻¹). This value supports the existance of the S = 3/2 [Ni₂(napy)₄]³⁺ unit and suggests that the spin state of the one-electron oxidized fragment is 1/2.



Fig. 3 Plot of $\chi_m T$ versus T for 1. The solid line represents the theoretical fit.

Moreover, the $\chi_m T$ value decreases as the temperature lowers and reaches the minimum $(1.10 \text{ cm}^3 \text{ Kmol}^{-1})$ below 50 K, which indicates that the S = 3/2 and S = 1/2 centers are antiferromagnetically coupled and the ground state of **1** is S = 1. The magnetic susceptibility data were tentatively fitted by a simple isotropic Heisenberg model ($H = -2J_{AB}S_AS_B$)^{5a} with the development of the van Vleck equation appropriate to S_A = 3/2 and S_B = 1/2.^{5b} The best fit parameters are $g_{3/2} = 2.17$, $g_{1/2} = 2.21$ and J = -53.3 cm⁻¹, which shows antiferromagnetic interaction between S = 3/2 and S = 1/2 centers.

To gain more insight into the electronic structure of 1. DFT/B3LYP calculations were carried out on 1. For the sake of simplicity, the phenyl rings of phdptrany³⁻ were replaced by hydrogen atoms.⁶ The geometry of **1** was optimized in two spin states ${}^{5}A$ (S = 2) and ${}^{3}B$ (S = 1) for comparison (Scheme 2). The ⁵A state represents the charge disproportionate model, while the ³B state represents the charge localized model. The optimized bond distances of ⁵A and ³B states are displayed in Fig. 4. The computed geometry of the ³B state shows an elongated Ni(1)-Ni(2) bond length, which significantly deviates from the observed bond distance. On the contrary, the geometry optimized for the ⁵A state is in agreement with the observed structure, especially the trends of Ni(1)-Ni(2) and Ni(2)-N bond lengths.^{2a} Furthermore, the calculated Ni(5)-Ni(6) and Ni(6)-Ni(7) distances of the ⁵A state are shorter than those of ³B, correspondence with the experimental results. The calculated energy for the ⁵A state is lower by



Scheme 2 Two electronic configurations calculated for 1.



Fig. 4 Two electronic configurations calculated for 1; selected interatomic distances observed (bottom, plain), computed ${}^{5}A$ (middle, bold) and ${}^{3}B$ (top, italics) for 1.

Table 1 Details of the gross atomic spin orbital populations (α spin – β spin, electrons; Mulliken analysis) calculated for the high-spin ⁵A state of complex 1

	Nil	Ni2	Ni3	Ni4	Ni5	Ni6	Ni7
$\sigma^a \ \delta^b \ \pi^c$	0.58 0.83 0.03	0.40 0.81 0.03	0.06 0.01 0.00	0.09 0.00 0.00	0.26 0.00 0.01	0.35 0.03 0.01	0.18 0.02 0.00
$a^{a} d_{z^{2}}$ popu	spin popu ilation.	ilation. ^b	$d_{x^2-y^2} + a$	d _{xy} spin po	opulation	$d_{\rm xz} + d_{\rm xz}$	d _{yz} spin

0.63 eV than that for the ${}^{3}B$ state. This substantial energy difference and the ideal optimized structure of ⁵A suggests that the charge disproportionate model of 1 is indeed more stable, which results in self-redox reactions of nickel ions in the period of synthesis. It is noteworthy that the approximation of the antiferromagnetic state (S = 1) of **1** by performing the broken symmetry (BS) approach⁷ is unsuccessful, which might be attributed to the fact that compound 1 contains two different MV systems, $(Ni_2)^{3+}$ and $(Ni_3)^{7+}$. Since the BS approach is typically based on a pure Heisenberg system, a comprehensive treatment of the BS state of 1 is far beyond the possibilities of the BS approach.^{2a} The spin distribution of the ${}^{5}A$ state shows 1.44 e on the terminal Ni(1) and 1.24 e on Ni(2), which exhibits the partial delocalized behaviour.^{2a} It appears from a more detailed analysis (Table 1) that this partial delocalization occurs along the metal axis through a transfer of a β-spin electron density from Ni(2) to Ni(1) in 1, and leads to the formation of a three-electron-two-centre σ bond.^{2a} Furthermore, the spin distribution on the terminal Ni(5)-Ni(6)-Ni(7) unit mainly concentrates on the d_{z^2} orbitals, which indicates that the delocalization of β -spin electrons through the σ pathway within the $(Ni_3)^{7+}$ unit (Scheme 2, top). This delocalization results from the formation of a nickel–nickel σ bond, since the σ^* spin density was depopulated upon one-electron oxidation.⁴ The related Ni-Ni distances of 1, therefore, are shorter than those of its analogue.^{2b} It is interesting to note that the spin densities on closed-shell Ni(3) and Ni(4) are slightly positive, which indicates the electronic communication between $(Ni_2)^{3+}$ and the $(Ni_3)^{7+}$ terminus. This electronic communication provides a pathway for AF interaction and enhances the electron mobility within whole heptanickel framework.

In summary, we have synthesized and characterized the longest asymmetric heptanickel string complex. The metal framework of 1 contains two different MV units, $(Ni_2)^{3+}$ and $(Ni_3)^{7+}$, due to its one-electron reduction and oxidation. It is the first example of metal string complexes that possesses this unusual *charge disproportionate metal chain*. Moreover, the spin distribution of 1 shows that the $(Ni_2)^{3+}$ and $(Ni_3)^{7+}$ terminus are electronically coupled. This behaviour suggests that compound 1 not only contains two MV $(Ni_2)^{3+}$ and $(Ni_3)^{7+}$ units, but also possesses a third extended MV $[(Ni_2)^{3+}-(Ni_3)^{7+}]$ system. Since mixed-valent units had been proved to be a conductance-enhanced material,^{2a} this extended MV $[(Ni_2)^{3+}-(Ni_3)^{7+}]$ system of 1 is expected to exhibit higher electronic conductance than traditional MV nickel strings do. It is noteworthy that because of the electronic

asymmetry results from charge disproportionation, complex 1 might also have a potential application as a molecular rectifier.^{2c,8}

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Notes and references

§ Crystal data for 1: Ni₇C₁₀₆H₈₆N₂₈Cl₉PF₆, $M_w = 2627.02$, monoclinic, space group $P2_1/c$, a = 41.262(2) Å, b = 13.7958(7) Å, c = 18.5806(9) Å, $\alpha = 90^{\circ}$, $\beta = 99.7034(1)^{\circ}$, $\gamma = 90^{\circ}$, V = 10425.5(9) Å³, Z = 4, $d_{\text{(calcd)}} = 1.674$ Mg m⁻³, T = 150(2) K, 49140 reflection collected, 18168 independent, $R_{\text{int}} = 0.1020$, $R_1 = 0.0664$, w $R_2 = 0.1570$ for all data.

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- 5 (a) M. Yonemura, Y. Matsumura, H. Furutachi, H. Õkawa and D. E. Fenton, *Inorg. Chem.*, 1997, **36**, 2711; (b) For two magnetic centres with $S_A = 3/2$, $S_B = 1/2$, the van Vleck equation can be developed as:

$$\chi_{\rm M} = \frac{N\beta^2}{kT} \frac{10g_2^2 \exp(-4J/kT) + 2g_1^2 \exp(-4J/kT)}{5 + 3\exp(-4J/kT)}$$

in which N is Avogadro's constant, g is the Lande factor, β is the Bohr magneton, k is the Boltzmann constant, T is temperature and g_1 and g_2 are g factors associated with the total spin states $S_T = 1$ and 2, respectively. The g factors were expressed using the local $g_{3/2}$ and $g_{1/2}$ values as follows: $g_1 = (5g_{3/2} - g_{1/2})/4$ and $g_2 = (3g_{3/2} + g_{1/2})/4$.

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