

Supporting Information

Further studies of $[\text{Ni}_4(\text{DAniDANy})_4]$ and Its One-Electron Oxidation Product : Metal-Metal Sigma Bonding in Ni_4^{9+} Complex

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Materials

All reagents and solvents were purchased from commercial sources and were used as received unless otherwise noted. The $\text{H}_2\text{DAniDANy}$ ligand and tetranickel string, $[\text{Ni}_4(\text{DAniDANy})_4]$ (**1**), were prepared according to the literature procedures.[1]

Physical Measurements

FAB mass spectra were obtained with a JEOL HX-110 HF double-focusing spectrometer operating in the positive ion detection mode. Magnetic susceptibility values were collected with a Quantum external magnetic field of 3000 G. EPR spectra were monitored with a Bruker EMX-10. Samples were run at 9.49 GHz (X-band) at 77 K. Electrochemistry measurements were carried out with a CH Instruments equipment (Model 750A) with the use of CH_2Cl_2 as the solvent with 0.1 TBAP and 1 mM analytes. Cyclic voltammetry was recorded with a homemade three-electrode cell equipped with a BAS glossy carbon (0.07 cm^2) disk as the working electrode, a platinum wire as the auxiliary electrode, and a homemade Ag/AgCl (saturated) reference electrode. The reference electrode was separated from the bulk solution by a

double junction filled with electrolyte solution. Potentials are reported versus Ag/AgCl (saturated) and referenced to the ferrocene–ferrocenium ($[\text{Cp}_2\text{Fe}]/[\text{Cp}_2\text{Fe}]^+$) couple, which occurs at $E_{1/2} = +0.54 \text{ V}$ vs. Ag/AgCl (saturated). The working electrode was polished with 0.03 μm alumina on Buehler felt pads and was subjected to ultrasound for 1 min prior to each experiment. The reproducibility of individual potential values was within $\pm 5 \text{ mV}$. Optically transparent thin-layer electrochemical electrode (OTTLE) spectra were accomplished with the use of a 1 mm thick UV cell, a 100-mesh platinum gauze as working electrode, a platinum wire as auxiliary electrode, and a Ag/AgCl (saturated) reference electrode.

Synthesis

$[\text{Ni}_4(\mu_4\text{-DAniDANy})_4](\text{PF}_6)_4$ (**2**):

In a flask, compound **1** (171.6 mg, 0.1 mol) and ferrocenium hexafluorophosphate (33.1 mg, mol) were dissolved in CH_2Cl_2 (50 mL) and stirred for 1 h. The mixture was then filtered. The filtrate was condensed to 5 mL and precipitated with ether. Single crystals suitable for X-ray diffraction studies were obtained via layer of $\text{CHCl}_2\text{CH}_2\text{Cl}$ (1,1',2-trichloroethane) with hexane. Yield : 101 mg, 53%. MS(FAB) m/z : 1715 ($[\text{Ni}_4(\text{DAniDANy})_4]^+$).

X-Ray crystallographic determinations

The crystals were mounted on a glass fiber. Crystal data were collected on a NONIUS Kappa CCD diffractometer with monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at $T = 150(2) \text{ K}$ for **2**. Cell parameters were retrieved and refined using *DENZOSMN* software on all observed reflections. Data reduction was performed with the *DENZO-SMN* software.[2] An empirical absorption was based on the symmetry-equivalent reflections and absorption corrections were applied with the

SORTAV program.[2] All the structures were solved by using the *SHELXS-97* and refined with *SHELXL-97* by full-matrix least squares on F^2 values.[2] Hydrogen atoms were fixed at calculated positions and refined using a riding mode. Asymmetric unit in the crystal structure contains 1/4 $[\text{Ni}_4(\text{DAniDANy})_4]^+$ cation. The $[\text{Ni}_4(\text{DAniDANy})_4]^+$ cation locates at two-fold axis and one mirror plane with 50% disorder of a spiral set of four DAniDANy^{2-} ligands.

Table S1: Crystal data and structure refinement for $[\text{Ni}_4(\mu_4\text{-DAniDANy})_4](\text{PF}_6)$ (**2**)

$2 \cdot 4\text{CHCl}_2\text{CH}_2\text{Cl}$	
formula	$\text{C}_{96}\text{H}_{84}\text{Cl}_{12}\text{F}_6\text{Ni}_4\text{O}_8\text{P}$
fw	2395.00
Temperature (K)	150(2)
crystal system	Orthorhombic
space group	$C2/m$
a (Å)	16.9785(9)
b (Å)	22.6333(12)
c (Å)	13.0677(7)
α (°)	90
β (°)	90.7910(10)
γ (°)	90
V (Å ³) / Z	5021(2) / 2
R_F, R_{wF}^2 ($I > 2\sigma(I)$) ^a	0.0902, 0.2340
R_F, R_{wF}^2 (all data) ^a	0.1257, 0.2622

$$^a R_F = \sum |F_o - F_c| / \sum |F_o|; R_{wF}^2 = [\sum w |F_o^2 - F_c^2|^2 / \sum w F_o^4]^{1/2}$$

Calculations: Calculations on compounds **1** and **2** have been carried out using the Density Functional Theory (DFT) in the ORCA software.[3] Full geometry optimizations were carried out with the BP86 functional in the gas phase [4]. The TZVP (for Ni and N atoms), and SVP (for other atoms) basis sets were applied in combination with the TZV/J (Ni and N atoms) and SV/J (remaining) auxiliary basis sets.[5] The RI approximation was used to accelerate the calculations.[5, 6]

References

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