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A Trinickel Dipyridylamido Complex with Metal−Metal Bonding Interaction: Prelude to Polynickel Molecular Wires and Devices?

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It has been known for many years that dinuclear compounds of the paddlewheel structure show a remarkable richness in their electrochemistry, and it is not unusual to find one or two redox waves.[1] For many of these dimetal units, however, the isolation of the oxidized M_2^{5+} or M_2^{6+} has been challenging. For example, in the case of the well-studied quadruply bonded dimolybdenum carboxylates, it was only recently that the first structures of one electron oxidation products were reported.[2]

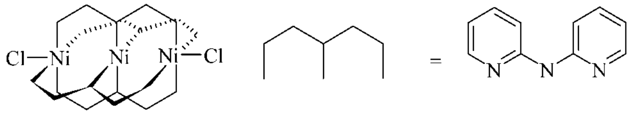
It is also well established that some electron rich M_2^{4+} units such as Pt_2^{4+} (with no metal−metal bond) can be oxidized to Pt_2^{6+}.[1] The removal of the two antibonding electrons gives rise to a diplatinum unit with a single σ bond. Recently, the first paddlewheel compound with the singly bonded Pd_2^{6+} unit was also synthesized in our laboratory.[3] In our earlier work, we also prepared the only known Ni_2^{5+} paddlewheel complex, $Ni_2(DTolF)_4BF_4$ (DTolF = *N,N'*-di-*p*-tolylformamidinate), which has a bond order of 0.5.[4] This compound was generated by the reaction of $AgBF_4$ and $Ni_2(DTolF)_4$, the latter having two noninteracting square-planar Ni^{II} atoms. Upon oxidation, the Ni−Ni separation of 2.485(2) Å decreases to 2.418(4) Å.

We have recently extended our research on compounds with metal−metal bonds to include linear trimetal[5,6] units, and compounds with higher nuclearity,[7] especially the electrochemistry and chemical oxidation of the trichromium compounds,[8] which were discovered in this laboratory, and the tricobalt[9] compounds. We now turn our attention to trinickel compounds.

The compound $Ni_3(dpa)_4Cl_2$ (**1**, dpa = di-2,2′-pyridylamide) was first synthesized in 1968,[10] but its structure remained a mystery until 23 years later when it was shown to be that depicted in Scheme 1.[11] It has subsequently been found that dipyridylamido complexes of other metals also adopt this structure.[12] Even though this compound was the first known of its type, its chemistry has been relatively unexplored.

Our original study[13] of **1** showed the compound to be paramagnetic, the terminal five-coordinate Ni^{II} atoms each having two unpaired electrons. Also, we concluded that there is no formal metal−metal bonding, even though the Ni···Ni separations are relatively short (∼2.43 Å). In this connection it is important to mention the extensive work of Peng and co-workers, who have prepared homologous nickel compounds with five, seven, and nine nickel atoms in a linear array.[14] Their results abundantly support our view that there is an absence of net Ni−Ni bonding but an antiferromagnetic coupling of the magnetic moments on the terminal Ni atoms, though exactly how this coupling is accomplished remains to be clarified. We previously[13] pointed out the inapplicability of a delocalized MO electronic structure for **1**, and by an obvious extension for any of the Ni_n species (n = 3, 5, 7, 9, ...), because it would predict that they would all have diamagnetic ground states. In fact, they all have a pair of antiferromagnetically coupled high-spin Ni^{II} ions at the ends.[14]

Scheme 1



Since we have found in the past that we could oxidize dinickel units with formamidinate ligands,[4] we therefore suspected that one-electron oxidation of $Ni_3(dpa)_4Cl_2$ could be possible, and might yield oxidized products with net three-center metal−metal bonding. Here we report the oxidation of $Ni_3(dpa)_4Cl_2$ to $Ni_3(dpa)_4(PF_6)_3$ (**2**) (eq 1), the crystal structure of **2**·$5CH_2Cl_2$, and the magnetic properties of this compound.

$$Ni_3(dpa)_4Cl_2 + 3AgPF_6 \rightarrow Ni_3(dpa)_4(PF_6)_3 + 2AgCl + Ag \quad (1)$$

A cyclic voltammogram[15] (Figure S1) shows that **1** has only a single one-electron, reversible oxidation/reduction wave at $E_{1/2}$ = 0.908 V (vs the Ag/AgCl reference). Though the potential is high, it is not out of the range of common oxidants,[16] and it was found that $AgPF_6$ is a suitable reagent. Three equivalents of Ag^+ are necessary to obtain the desired product: 2 equiv to remove the axial chloride ligands and 1 equiv to perform the oxidation.

Although the dark blue compound **2** was isolated in 62% yield, it is unstable, quickly decomposing in solution at room temperature. Because of this, we have so far been unable to obtain its electronic spectrum or EPR spectrum. The solid is easier to handle, and we were able to perform an X-ray crystal structure determination[17] on a single crystal of the compound, as well as a measurement of the temperature dependence of the magnetic susceptibility of a bulk sample.[18]

The structure of **2** is shown in Figure 1. There are a pair of independent molecules, each on a position of 2-fold symmetry. The asymmetric unit thus consists of two unconnected halves of the molecule and five molecules of dichloromethane. For each Ni_3^{7+} unit there are two PF_6^- anions occupying axial positions and having weak Ni···F interactions (Ni···F distances are over 2.4 Å). The most arresting feature of the structure is the extremely short Ni−Ni distance of 2.283[1] Å, compared to ca. 2.43 Å in **1**.

It is useful here to compare the geometry of **2** to that of **1**. Our earlier report of compound **1** gives the relevant data for that compound.[13] The most striking difference is the change in Ni−Ni distances. In compound **2**, the Ni−Ni distances are shorter by 0.16

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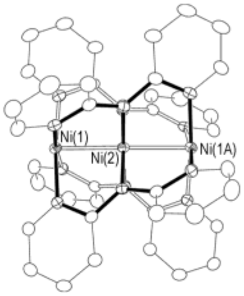

Figure 1. Perspective view of one of the two crystallographically independent $Ni_3(dpa)_4{}^{3+}$ cations with thermal ellipsoids drawn at 30% probability. The bold bonds were drawn to aid visualization. The hydrogen atoms, counterions, and solvent molecules are omitted for clarity. Relevant bond distances: Ni−Ni 2.284[1] Å, outer Ni−N 1.927[5] Å, inner Ni−N 1.881[5] Å. Overall torsion angle 46.1°.

Å, clearly indicative of the formation of a partial nickel−nickel bond. Also, the outer Ni−N distances are shorter in **2**, due to the stronger attraction of the ligand to the highly positive $Ni_3{}^{7+}$ core. The central Ni−N distances are only ~0.05 Å shorter than the outer Ni−N distances, as compared to the ~0.22 Å difference in **1**.

Let us also compare this change in geometry with that reported with the one-electron oxidation of $Ni_2(DTolF)_4$.[4] Upon oxidation, the Ni−Ni distance in the $Ni_2(DTolF)_4$ unit became shorter by 0.07 Å, a much less pronounced change than that reported here for the trinuclear system, even though in the former case the loss of one electron affects only one Ni−Ni pair whereas here it affects two.

The magnetic data for **2** obey the Curie law. A plot of $1/\chi$ vs T is shown in Figure S2. The temperature-independent value, $\chi T = 0.5204$ emu·K·mol^{-1}, is consistent with one unpaired electron. This is a drastic change from the complex magnetic behavior of **1**.

We believe that the results reported here are very significant not only for linear trinickel compounds but also for any homologous Ni_5, Ni_7, or Ni_9 compounds which may also undergo one electron oxidation. What has, very surprisingly, happened in the present case is that on oxidizing $Ni_3(dpa)_4Cl_2$ to $Ni_3(dpa)_4(PF_6)_3$, the electronic structure of the central Ni_3 unit has been profoundly changed. Instead of (to a very useful approximation) an array of three Ni^{2+} ions with the outer two being high-spin and the inner one being diamagnetic, maintained in moderately close proximity by the four bridging ligands, we have now a $Ni_3{}^{7+}$ unit, within which there is delocalized metal−metal bonding. We venture the prediction that similar changes (i.e., conversion to delocalized systems with one unpaired electron) will take place in the oxidation of $Ni_5{}^{10+}$, $Ni_7{}^{14+}$, and $Ni_9{}^{18+}$ (and ultimately all $Ni_n{}^{2n+}$) systems. This will probably allow them to function as molecular wires,[19] whereas the neutral $Ni_n{}^{2n+}$ molecules are unlikely to do so.

We recognize that if it is correct to assume that the neutral $Ni_n{}^{2n+}$ complexes are nonconducting and the ionic $Ni_n{}^{(2n+1)+}$ complexes will be conductors (or, at least, that there will be a marked change in conductance upon oxidation), there is the clear potential for employing such compounds as diode-like elements in nanoscale circuitry.[20]

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Supporting Information Available: Figure S1 (cyclic voltammogram of **1**), Figure S2 (magnetic measurement of **2**), synthetic procedure, and a fully labeled drawing of each independent molecule (PDF) and crystal data for $\mathbf{2}\cdot 5CH_2Cl_2$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Electrochemistry: The solution was 1 M NBu_4PF_6, 0.1 mM $Ni_3(dpa)_4Cl_2$, and ~0.1 mM ferrocene in dichloromethane. The electrodes were the following: Pt disk (working), Pt wire (auxiliary), and Ag/AgCl reference. The $E_{1/2}$ for ferrocene in this system was 0.422 V.

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(18) Data points were taken with a field of 1000 G as the temperature swept from 2 to 300 K on a Quantum Design SQUID magnetometer MPMS-XL, and data were corrected for diamagnetism prior to analysis.

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