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Article

Oxidation of $Ni_3(dpa)_4Cl_2$ and $Cu_3(dpa)_4Cl_2$: Nickel–Nickel Bonding Interaction, but No Copper–Copper Bonds

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Of the known trinuclear dipyridylamido complexes of the first-row transition metals, $M_3(dpa)_4Cl_2$ (dpa is the anion of di(2-pyridyl)amine, M = Cr, Co, Ni, Cu), the one-electron-oxidation products of only $Cr_3(dpa)_4Cl_2$ and $Co_3(dpa)_4Cl_2$ have been isolated previously. Here we report one-electron-oxidation products of $Ni_3(dpa)_4Cl_2$ (**1**) and $Cu_3(dpa)_4Cl_2$ (**3**): $Ni_3(dpa)_4(PF_6)_3$ (**2**) and $[Cu_3(dpa)_4Cl_2]SbCl_6$ (**4**). While there are no Ni–Ni bonds in **1**, the Ni–Ni distances in **2** are 0.15 Å shorter than those in **1**, very suggestive of metal–metal bonding interactions. In contrast, the oxidation of **3** to **4** is accompanied by a lengthening of the Cu–Cu distances, as expected for an increase in electrostatic charge between positively charged nonbonded metal ions, which is further evidence against Cu–Cu bonding in either **3** or **4**. A qualitative model of the electronic structures of all $[M_3(dpa)_4Cl_2]^{n+}$ ($n = 0, 1$) compounds is presented and discussed.

Introduction

Di(2-pyridyl)amine (Hdpa) has been shown to stabilize linear trinuclear coordination compounds of four first-row transition metals (Cr,[1] Co,[2] Ni,[3] Cu[4]) and two second-row transition metals (Ru and Rh).[5] These trinuclear molecules are the simplest prototypical examples of a very large class of compounds having *extended metal atom chains* (EMACs). Using appropriate ligands, chains of higher nuclearity can be obtained.[6,7] While the work of S.-M. Peng's laboratory has focused on creating longer linear chains of metal atoms,[7] our main goal has been to elucidate the fundamental properties of the trinuclear compounds, especially their electronic structures. We have done this because we believe that there is little chance of understanding longer EMACs until we can understand the prototypical ones.

By studying the electronic properties of these compounds and their one-electron-oxidation products, we have found startling variability in the propensity for the compounds to have a localized or delocalized electronic structure. For example, our initial study of $Ni_3(dpa)_4Cl_2$, **1**, led us to the conclusion that the d electrons of the trinickel chain are localized on the metal atoms to give a diamagnetic central atom and two outer ones in triplet states, which are antiferromagnetically coupled.[3a] Our preliminary report on the one-electron-oxidation product of this compound,[8] however, showed that the electronic structure changes dramatically, now having delocalized Ni−Ni bonding, with

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only one unpaired electron residing in a three-center σ antibonding orbital.

Further examples of the subtleties of the electronic structures of these three-atom chains are provided by $Cr_3(dpa)_4Cl_2$ and $Co_3(dpa)_4Cl_2$, which exist in symmetrical and unsymmetrical forms of D_4 and C_4 symmetry, respectively, the structure of the molecules depending on the method of crystallization.[2b,c,9] We proposed that the symmetrical forms have delocalized three-center metal−metal bonds, while the unsymmetrical forms consist of an M_2^{4+} unit and an isolated M^{2+} species, which are not bonded to each other. Furthermore, the one-electron-oxidation products of $Cr_3(dpa)_4Cl_2$[10] and $Co_3(dpa)_4Cl_2$[11] could not be more different. All six known $Cr_3(dpa)_4^{3+}$ compounds are distinctly unsymmetrical, to the extent that they can be said to consist of a Cr_2^{4+} quadruple bond and an isolated high-spin Cr^{3+} atom, the latter being responsible for the observed quartet ground state. In contrast, $Co_3(dpa)_4Cl_2^+$ has a symmetrical structure, and a delocalized model of its electronic structure explains very well its unique magnetic behavior. It is a very rare example of a compound that undergoes two stepwise thermal spin-crossover transitions.[11]

Calculations at the density functional level of theory carried out by Rohmer, Bénard, and co-workers[12] rationalize some of our experimental findings in the case of $Co_3(dpa)_4Cl_2$, but fail to account for *why* the compound can exist in two drastically different forms.[12a,b] Their work on the electronic structure of $Cr_3(dpa)_4Cl_2$ is also useful, but again does not answer the question of *why* the compound can exist in both symmetrical and unsymmetrical forms.[12c]

Here we provide a complete report on the one-electron-oxidation product of $Ni_3(dpa)_4Cl_2$ (**1**): $Ni_3(dpa)_4(PF_6)_3$ (**2**). We also characterize the corresponding oxidation product of $Cu_3(dpa)_4Cl_2$ (**3**), $[Cu_3(dpa)_4Cl_2]SbCl_6$ (**4**). This is the first time that the $Cu_3(dpa)_4X_2$ system has been isolated with the Cu_3 unit in a formal oxidation state higher than 6+.

Experimental Section

General Information. All manipulations were carried out under an atmosphere of dry dinitrogen gas using standard Schlenk techniques. Solvents were distilled in a nitrogen atmosphere over appropriate drying agents prior to use. $Ni(Hdpa)_2Cl_2$ was made according to the method of Hurley and Robinson.[13] $Cu_3(dpa)_4Cl_2$ was prepared according to the method of Berry et al.[4a] Silver hexafluorophosphate was purchased from Strem Chemicals and was used as received. Tris(*p*-bromophenyl)aminium hexachloroantimonate was used as received from Aldrich and was stored in the dark.

Physical Measurements. Measurements were taken on polycrystalline samples from which the interstitial solvents had been removed under vacuum overnight. IR spectra were taken on a Perkin-Elmer 16PC FTIR spectrometer using the KBr pellet technique. X-band EPR spectra were obtained on a Bruker ESP 300 spectrometer. UV−vis spectra were recorded on a Cary 17 spectrophotometer on dichloromethane solutions. Electronic reflectance spectra were obtained in the region from 400 to 1000 nm on a HP 845x UV−visible system with a Labsphere RSA-HP-8453 reflectance spectroscopy accessory. Elemental analyses were carried out by Canadian Microanalytical Services in British Columbia, Canada. They were satisfactory for **2**, but not for **4**. Because of the temperature instability, some decomposition of **4** occurred during shipment.

Magnetic susceptibility measurements for **4** were made on a polycrystalline sample which was placed in a plastic bag and mounted inside an ordinary drinking straw. The straw was then placed inside of a Quantum Design SQUID magnetometer MPMS-XL. The sample was centered at 300 K in the instrument, and data points were taken from 2 to 400 K at a field of 1000 G. The data were corrected empirically for the diamagnetism of the bag and sample.

For the electrochemical study, a solution of 1 M NBu_4PF_6, 0.1 mM **1** or **3**, and 0.1 mM ferrocene in dichloromethane was used. The electrodes were Pt disk (working), Pt wire (auxiliary), and Ag/AgCl (reference). The reversible wave for the **1**/**1**$^+$ couple appeared at 0.908 V, and the reversible wave for the **3**/**3**$^+$ couple was seen at 0.828 V. The $E_{1/2}$ for ferrocene in this system was 0.422 V for **1** and 0.4355 V for **3**.

$Ni_3(dpa)_4Cl_2$, 1. A pale bright blue suspension of $Ni(Hdpa)_2Cl_2$ (2.83 g, 6.00 mmol) in 60 mL of THF was cooled to −78 °C by means of a dry ice/acetone cooling bath. To this suspension was added slowly 5.0 mL of a solution of 1.6 M methyllithium in diethyl ether (4.0 mmol), which caused the suspension to become lime green in color. The suspension was then allowed to warm to room temperature, at which point it became dark brown. After stirring at room temperature for $^1/_2$ h, the brown mixture was heated to reflux overnight, giving a dark purple mixture. The solvent was removed under reduced pressure, leaving a dark purple residue. Upon extraction of this solid with dichloromethane, a purple solution resulted, from which the dark purple-red product was crystallized by diffusion of hexanes. Yield: 1.2 g, 65%. IR (KBr, cm^{-1}): 3448.1 (m, br), 1655.2 (w), 1637.6 (w), 1602.3 (s), 1592.3 (s), 1548.8 (m), 1466.9 (vs), 1423.1 (vs), 1364.2 (m), 1354.0 (m), 1311.0 (m), 1282.0 (m), 1241.0 (w), 1153.8 (m), 1052.0 (w), 1013.4 (m), 925.9 (vw), 891.1 (w), 764.1 (s), 739.5 (m), 685.4 (w), 639.3 (w), 516.9 (w), 427.2 (w). UV−vis (CH_2Cl_2: λ_{max} (nm), ϵ (M^{-1} cm^{-1})): 520, 2650; 376 (sh), 12700; 341, 46600; 312, 50400; 248, 38000.

$Ni_3(dpa)_4(PF_6)_3$, 2. To a flask containing 100 mg of **1** (0.108 mmol) and 82 mg of $AgPF_6$ (0.323 mmol) was added 19 mL of freshly distilled and degassed dichloromethane at −78 °C. The initially reddish-purple solution became dark blue upon stirring, and a gray precipitate formed. The cold solution was filtered through Celite into a crystallization tube, also kept at −78 °C. The solution was layered with cold hexanes, and kept in a freezer at −20 °C, where wedge-shaped crystals grew within a few days. Dark-blue crystals were recovered: 85.3 mg, 62% yield. IR (KBr, cm^{-1}): 3422.5 (m, br), 1655.4 (m), 1606.3 (s), 1560.9 (w), 1471.7 (vs), 1427.1 (vs), 1364.9 (m), 1312.9 (m), 1292.3 (m), 1262.9 (m), 1242.7 (w), 1157.4 (s), 1098.7 (s), 1030.0 (m), 842.5 (s), 764.1 (m), 741.3 (m), 693.8 (vw), 557.9 (m), 483.1 (m), 397.7 (m). Anal. Calcd for $Ni_3C_{40}H_{32}N_{12}P_3F_{18}$: C, 37.18; H, 2.48; N, 13.01. Found: C, 37.67;

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H, 2.77; N, 13.04. Visible reflectance (λ_{max}, nm): 580. Near-IR (CH_2Cl_2 solution: λ_{max} (nm), ϵ (M^{-1} cm^{-1})): 1045, 7800.

$[Cu_3(dpa)_4Cl_2]SbCl_6$, 4. A flask containing 200 mg of **3** (0.212 mmol) and 173 mg of tris(*p*-bromophenyl)aminium hexachloroantimonate (0.212 mmol) was charged in the dark with 20 mL of toluene. The solution was stirred at room temperature in the dark for 3 h, at which time a red precipitate was observed. The precipitate was collected by filtration, washed with toluene (2 × 30 mL), and dried under vacuum. Yield: 250 mg, 92%. Large block-shaped crystals of **4**$\cdot 2.86C_2H_4Cl_2\cdot 0.792C_6H_{12}$ were readily grown by dissolving the red solid in 1,2-dichloroethane at −78 °C and layering the solution with cyclohexane. Large crystalline needles of **4**$\cdot 2.44C_3H_6O$ were grown by diffusion of hexanes into an acetone solution of **4**. IR (KBr, cm^{-1}): 3448.0 (m, br), 3066.9 (w), 1596.9 (m), 1466.9 (vs), 1459.0 (s), 1425.2 (vs), 1365.9 (m), 1312.8 (W), 1286.7 (w), 1235.8 (m), 1157.9 (m), 1096.6 (w, br), 1013.7 (m), 802.7 (w), 761.7 (m), 736.1 (w), 641.2 (w), 432.5 (w). UV−vis−NIR (CH_2Cl_2 solution: λ_{max} (nm), ϵ (M^{-1} cm^{-1})): 247, 38000; 281, 35700; 323, 41400; 349 (sh), 19900; 372 (sh), 6230; 487, 4910; 704, 925; 1316, 574. Anal. Calcd for $Cu_3C_{40}H_{32}N_{12}Cl_8Sb$: C, 37.62; H, 2.51; N, 13.17. Found: C, 37.79; H, 2.48; N, 11.86.

X-ray Crystallographic Determinations. Geometric and intensity data for **1**$\cdot Et_2O$ and **1**$\cdot$2toluene$\cdot$0.5hexane were collected on a Nonius FAST four-circle area detector system at −60 °C, utilizing the software program MADNES.[14] In each case, a unit cell was refined from 250 strong reflections with $18.1° < 2\theta < 41.8°$. The cell dimensions and Laue symmetry were confirmed from axial images. The data were corrected for Lorentz and polarization effects. The program PROCOR[15] was used to process the integrated data into SHELX format; SORTAV[16] was used to correct for absorption.

For **2**$\cdot 5CH_2Cl_2$ and **4**$\cdot 2.86C_2H_4Cl_2\cdot 0.792C_6H_{12}$, the data were collected on a Bruker SMART 1000 CCD detector system at −60 °C, using the SMART[17] software. Initial cell parameters were obtained from SMART. Data integration, correction for Lorentz and polarization effects, and final cell refinement were performed by SAINTPLUS.[18] The data were further corrected for absorption by SADABS.[19]

The crystals of **4**$\cdot 2.44C_3H_6O$ were twinned by a 180° rotation around [100] and followed the twin law:

$$h_1 = \begin{bmatrix} 1 & 0.001 & 0 \\ 0.001 & -1 & 0 \\ -0.732 & -0.004 & -1 \end{bmatrix} \cdot h_2$$

where h_1 and h_2 are the orientation matrices for the two twin components. Thus, the apparent *c* axis was twice the actual length, making the two twin components impossible to deconvolute from data collected on a normal area detector diffractometer.[20] Therefore, data were collected on a Rigaku R-AXIS RAPID diffractometer housed at Rigaku/MSC using the CrystalClear/TwinSolve software for data collection and processing.[21] By using Cu Kα radiation and taking advantage of the curved image plate detector of the RAPID (which has a 2θ range of −60° to +144°) the two twin components could be separated. The data were transformed to SHELX HKLF 5 format so that both twin components could be refined simultaneously.[22]

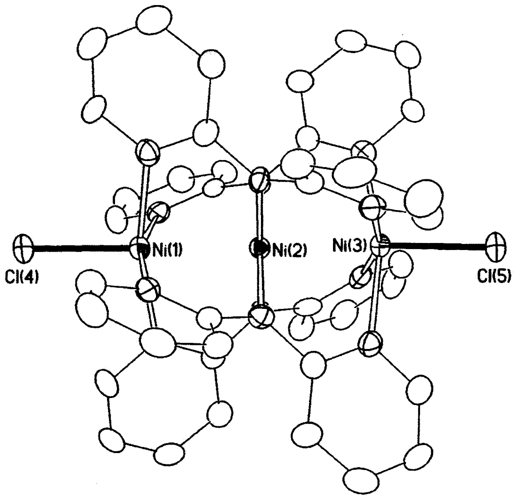

Figure 1. Displacement ellipsoid plot of **1** in **1**$\cdot$Et2O. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

For each data set, the initial solution was performed by the direct methods program in SHELXTL.[23] Subsequent refinement cycles (refined on F^2) and Fourier synthesis revealed the positions of all of the atoms. There were some difficulties in the refinement of **4**$\cdot 2.86C_2H_4Cl_2\cdot 0.792C_6H_{12}$ in that a large peak (>2 e/Å^3) appeared near one of the pyridyl carbon atoms. Due to the position of the peak (<1 Å from a hydrogen atom), it is physically impossible for it to be an actual atom. For **4**$\cdot 2.44C_3H_6O$, the HKLF 5 data gave the proper solution with no ghost peaks. It is likely that **4**$\cdot 2.86C_2H_4Cl_2\cdot 0.792C_6H_{12}$ could suffer from twinning as for **4**$\cdot 2.44C_3H_6O$, but this has not been confirmed. Importantly, both crystal structures containing **4** have the same core structure, and the interatomic distances are in agreement. For practical purposes, the distances in **4**$\cdot 2.44C_3H_6O$ are used in further comparisons.

Drawings of compounds **1**$\cdot Et_2O$, **2**$\cdot 5CH_2Cl_2$, and **4**$\cdot 2.44C_3H_6O$ are shown in Figures 1, 2, and 3, respectively. Table 1 summarizes the crystallographic data. Table 2 contains a list of selected bond distances and angles for **1**$\cdot Et_2O$ and **1**$\cdot$2toluene$\cdot$0.5hexane, as well as those previously reported for other crystal forms. Table 3 contains a list of selected bond distances and angles for **2**$\cdot 5CH_2Cl_2$, and Table 4 contains a list of selected bond distances and angles for **4**$\cdot 2.86C_2H_4Cl_2\cdot 0.792C_6H_{12}$ and **4**$\cdot 2.44C_3H_6O$.

Results

$M_3(dpa)_4Cl_2$ compounds are known to exist in different crystal forms depending on the method of crystallization. In some cases where M−M bonds are present, this may affect

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(14) Pflugrath, J.; Messerschmitt, A. *MADNES*, Munich Area Detector (New EEC) System, Version EEC 11/1/89, with enhancements by Enraf-Nonius Corp., Delft, The Netherlands. A description of MADNES appears in the following: Messerschmitt, A.; Pflugrath, J. *J. Appl. Crystallogr.* **1987**, *20*, 306.

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(16) SORTAV. Program for absorption correction for Enraf-Nonius FAST diffractometer using the method of Blessing: Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

(17) *SMART V5.05 Software for the CCD Detector System*; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1998.

(18) *SAINTPLUS, V5.00 Software for the CCD Detector System*; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1998.

(19) *SADABS*. Program for absorption correction using SMART CCD based on the method of R. H. Blessing. See ref 16.

(20) Refinement from data gathered on a Bruker SMART 1000, for example, gave large (>2 e/Å^3) peaks surrounding the molecule in physically meaningless positions.

(21) CrystalClear: *An Integrated Program for the Collection and Processing of Area Detector Data*; Rigaku/MSC, Inc.: The Woodlands, TX, 1997−2002.

(22) Refinement of only one component using HKLF 4 data was still unsatisfactory since *all h* = 0 reflections overlap exactly from both twin components.

(23) *SHELXTL, Version 5.03;* Siemens Industrial Automation Inc.; Madison, WI, 1994.

Table 1. Crystal Data

	1·Et_2O	**1**·2toluene·0.5hexane	**2**·$5CH_2Cl_2$	**4**·$2.86C_2H_4Cl_2$·$0.792C_6H_{12}$	**4**·$2.44C_3H_6O$
formula	$C_{44}H_{42}Cl_2N_{12}Ni_3O$	$C_{57}H_{55}Cl_2N_{12}Ni_3$	$C_{45}H_{42}Cl_{10}F_{18}N_{12}Ni_3P_3$	$C_{48.33}H_{48.67}N_{12}Cl_{11.58}Cu_3Sb$	$C_{47.31}H_{46.63}Cl_8Cu_3N_{12}O_{2.44}Sb$
fw	1001.93	1155.16	1716.45	1520.54	1418.31
cryst syst	monoclinic	triclinic	monoclinic	tetragonal	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2/n$	$I4/m$	$P2_1/c$
a, Å	15.953(1)	16.991(2)	23.072(2)	29.937(1)	15.033(1)
b, Å	15.779(8)	18.211(2)	11.834(1)	29.937(1)	12.401(1)
c, Å	17.108(5)	19.138(3)	25.771(2)	28.151(3)	33.114(3)
α, deg	90	80.277(5)	90	90	90
β, deg	97.365(5)	81.847(8)	111.834(2)	90	99.506(3)
γ, deg	90	63.449(6)	90	90	90
V, Å^3	4271.1(4)	5206(1)	6546(1)	25229(3)	6088.5(9)
Z	4	4	4	16	4
d(calc), g cm^{-3}	1.558	1.474	1.742	1.601	1.547
R1,[a] wR2[b] ($I > 2\sigma(I)$)	0.0808, 0.2028	0.0539, 0.1330	0.0612, 0.1503	0.0674, 0.1789	0.1087, 0.2152
R1,[a] wR2[b] (all data)	0.1049, 0.2296	0.0659, 0.1440	0.0730, 0.1589	0.0878, 0.1927	0.1457, 0.2416

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3$.

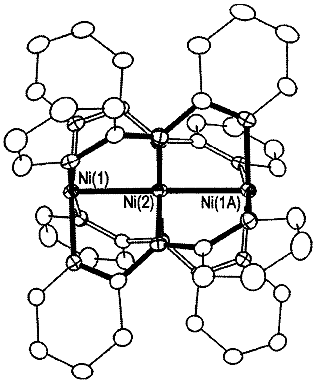


Figure 2. Displacement ellipsoid plot of the cation $Ni_3(dpa)_4^{3+}$ in **2**·$5CH_2Cl_2$. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

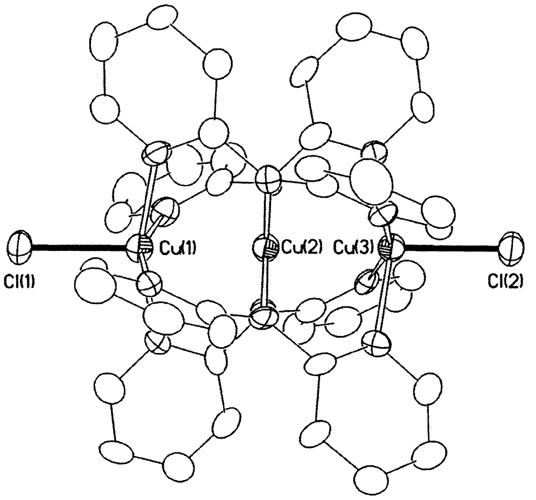


Figure 3. Thermal ellipsoid plot of the cation $Cu_3(dpa)_4Cl_2^+$ in **4**·$2.44C_3H_6O$. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

Table 2. Selected Interatomic Distances[a] for $Ni_3(dpa)_4Cl_2$

	1·Et_2O	**1**·2toluene·0.5hexane	**1**·$2CH_2Cl_2$[b]	**1**·THF[b]	**1**·$0.23H_2O$·0.5acetone[c]
Ni1···Ni2	2.438(1)	2.4249(9)	2.4386(9)	2.4172(8)	2.443(1)
(Ni4···Ni5)		2.4265(9)			2.431(1)
Ni2···Ni 3	2.433(1)	2.4253(9)	2.422(1)		2.443(1)
(Ni5···Ni6)		2.4386(9)			
$\mathrm{Ni_{outer}}$–N	2.087[6]	2.089[4]	2.09[9]	2.08[8]	1.89[9]
$\mathrm{Ni_{inner}}$–N	1.899[6]	1.889[4]	1.89[3]	1.89[6]	2.10[7]
Ni–Cl	2.328(2)	2.324(2)	2.348(2)	2.334(2)	2.340(2)
	2.348(2)	2.318(1)	2.336(2)		2.331(2)
		2.315(2)			2.325(3)
		2.348(1)			

[a] Distances given in angstroms. Numbers in square brackets correspond to average values. [b] Taken from ref 3a. Note that in **1**·THF, the molecule resides on a crystallographic 2-fold axis. [c] Taken from ref 3b. This crystal structure contains one entire molecule of **1** as well as another half molecule in the asymmetric unit. The second molecule is on a crystallographic 2-fold axis.

Table 3. Intermolecular Distances[a] of **2**·$5CH_2Cl_2$ (Å)

	2·$5CH_2Cl_2$
Ni1–Ni2	2.2851(6)
Ni3–Ni4	2.2885(7)
$\mathrm{Ni_{outer}}$–N	1.929[4]
$\mathrm{Ni_{inner}}$–N	1.881[4]
Ni···F	2.424(3)
	2.429(3)
P1–F1	1.646(3)
P2–F7	1.654(4)
P1–F(2–6), P2–F(8–12)	1.578[4]
P3–F	1.544[7]

[a] Numbers in brackets correspond to average values.

Table 4. Intermolecular Distances[a] for **4**

	4·$2.86C_2H_4Cl_2$·$0.792C_6H_{12}$	**4**·$2.44C_3H_6O$
Cu···Cu	2.513[1]	2.505[1]
$\mathrm{Cu_{outer}}$–N	2.065[6]	2.061[5]
$\mathrm{Cu_{inner}}$–N	1.886[6]	1.885[5]
Cu–Cl	2.388[2]	2.392[2]

[a] Numbers in brackets refer to averages.

significantly the separations between metal atoms. From Table 2, we see that the compound $Ni_3(dpa)_4Cl_2$ always has equal (or effectually equal) Ni–Ni distances. Though these are fairly short, there is no bond between the d^8 metal atoms.[3a] The Ni–N bond lengths of the four-coordinate central metal atom are significantly shorter than those from the outer five-coordinate nickel atoms, which is typical for this type of trinuclear compound having axial ligands. Two important factors are thought to be responsible for this: (1) the difference in the coordination number of the metal atoms; (2) the central nitrogen atom of the ligand being the atom which carries more of the negative charge (since this is the site of deprotonation).

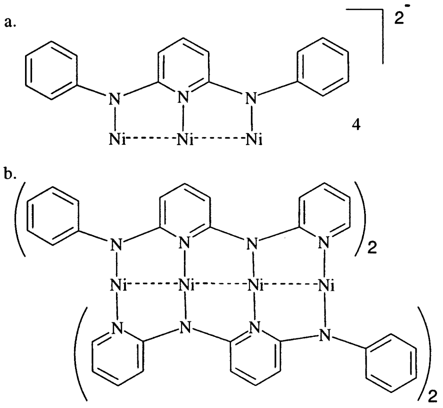
We recently synthesized a compound with a Ni_3^{6+} unit without axial ligands,[24] and found that all three of the Ni^{2+}

Table 5. Known Crystal Forms (with Metal−Metal Distances,[a] Å) of $M_3(dpa)_4Cl_2$ Compounds Depending on the Solvent of Crystallization

	*Pnn*2 $(M\cdot CH_2Cl_2)$[b]	$P2_1/c$ $(M\cdot Et_2O)$	$Pna2_1$ $(M\cdot C_6H_6)$	$Pca2_1$ $(M\cdot C_6H_6)$	$P\bar{4}n2$ $(M\cdot THF)$	$I\bar{4}$ $(M\cdot 2CH_2Cl_2)$	*Pccn* $(M\cdot THF)$	*Pccn* $(M\cdot C_6H_{12})$	$P\bar{1}$ $(M\cdot 1.75C_7H_8\cdot 0.5C_6H_{14})$	$C2/c$ $(M\cdot 0.23H_2O\cdot 0.5(CH_3)_2CO)$
$Cr_3(dpa)_4Cl_2$	2.366(1)[c]	2.249[4], 2.469[4][d]	2.296(2), 2.414(2); 2.326(2), 2.390(2)[c]	2.353(2), 2.365(2)[c]	2.365(2)[c]					
$Co_3(dpa)_4Cl_2$	2.3369(4)[h]	2.3193(3), 2.3352(3)[i]	2.323(1), 2.344(2); 2.326(2), 2.338(2)[i]			2.2943(9), 2.466(1)[h]	2.3111(4), 2.4402(7)[i]	2.3311(5), 2.436(1)[i]	2.3046(6), 2.4216(6); 2.3084(6), 2.3622(6)[i]	
$Ni_3(dpa)_4Cl_2$		2.436[1][g]				2.43[8][e]	2.4172(8)[e]		2.4251[9], 2.4326[9][g]	2.443[1], 2.431(1)[f]
$Cu_3(dpa)_4Cl_2$	2.471(1)[j,k]	2.470[8][k]		2.4699[9][k]						
$Ru_3(dpa)_4Cl_2$	2.2537(5)[l]									
$Rh_3(dpa)_4Cl_2$	2.3920(5)[l]									

[a] Metal−metal distances are arranged in order of short distance first followed by the longer one. Wherever two sets are given, those correspond to crystallographically independent molecules. Whenever only one is given, the second one is the same as required by symmetry. Also, brackets refer to average values. [b] M represents the corresponding $M_3(dpa)_4Cl_2$ species. [c] Reference 30. [d] Berry, J. F.; Cotton, F. A.; Murillo, C. A. Unpublished results. [e] Reference 3a. [f] Reference 3b. [g] This work. [h] Reference 2c. [i] Clerac, R.; Cotton, F. A.; Daniels, L. M.; Dunbar, K. R.; Murillo, C. A.; Wang, X. *Inorg. Chem.* **2001**, *40*, 1256. [j] Reference 4b. [k] Reference 4a. [l] Reference 5.

Scheme 1



ions are square planar (which also causes the compound to be diamagnetic), and all Ni−N distances are very similar. This is shown in Scheme 1a; it will be noted that the ligand here is a dianion. This result supports the above proposals, because here the three nickel atoms are four-coordinate and, in addition, the negative charges are formally on the outer nitrogen atoms. There is also a Ni_4 compound,[25] Scheme 1b, in which there is a completely equal distribution of formal charge and all nickel atoms are four-coordinate, and again in this case the inner and outer Ni−N bond lengths are equal to within 0.01 Å.

The helical structure is characteristic of all known $M_3(dpa)_4Cl_2$ compounds, independent of the solvent of crystallization, and examples are given in Table 5 along with the metal−metal separations. For $Co_3(dpa)_4Cl_2$ and $Cr_3(dpa)_4Cl_2$ it was found that the M−M distances vary widely among the different crystal forms. Most notably for $Cr_3(dpa)_4Cl_2$ there is a propensity for the compound to have a very unsymmetrical structure (consistent with the presence of a short quadruple bond between two chromium atoms, and an isolated Cr^{2+} unit at a longer distance), which is seen to a degree in $Co_3(dpa)_4Cl_2$ also. Even though some forms of the trichromium and tricobalt compounds are quite unsymmetrical, there exist crystal forms with equal or nearly equal metal−metal distances (see Table 5). This is not so for **1** and **3**. The Ni···Ni and Cu···Cu separations in all known crystal forms are similar (∼2.43 and ∼2.47 Å, respectively) and even when the two distances within the molecules are crystallographically independent, they are always nearly equal.

The crystal structure of **2** is remarkable mostly for its very short Ni−Ni separations, 2.28 Å. The change in Ni−Ni distances between **1** and **2** is 0.15 Å, clearly indicative of metal−metal bonding in the oxidized species (vide infra). The average Ni···F distances of 2.42 Å are long, but nonetheless the axial PF_6^- anions are highly distorted from their usual octahedral arrangement, having P1−F1 and P2−F7 much longer than the other P−F distances (1.65 vs 1.58 Å), which seems to show an avidity of the $Ni_3(dpa)_4^{3+}$ core for axial ligation. At first glance, this may appear to be contradictory: Why are the Ni···F separations so long *and* the PF_6 moieties distorted? We tried to answer this by preparing the neutral Ni_3^{6+} compound $Ni_3(dpa)_4(PF_6)_2$, but attempts to characterize this insoluble compound failed.[26] Presumably, this is because the PF_6^- anion is too bulky to fit in the axial position of the $Ni_3(dpa)_4^{2+}$ core, whereas the less sterically demanding BF_4^- anion has been shown to fit well, with M−F distances ranging from 2.27 to 2.38 Å for Cr,[27] Co,[2a] and Cu.[4a] From the distorted geometry of the axial PF_6^- ions in **2**, we can see that even though the $Ni_3(dpa)_4^{3+}$ core strongly pulls one of the P−F bonds in an attempt to have a ligand in the axial position, the PF_6 moiety as a whole

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(24) Cotton, F. A.; Daniels, L. M.; Lei, P.; Murillo, C. A.; Wang, X. *Inorg. Chem.* **2001**, *40*, 2778.

(25) Lai, S.-Y.; Lin, T.-W.; Chen, Y.-H.; Wang, C.-C.; Lee, G.-H.; Yang, M.-H.; Leung, M.-K.; Peng, S.-M. *J. Am. Chem. Soc.* **1999**, *121*, 250.

(26) $Ni_3(dpa)_4(PF_6)_2$ does, however, dissolve in acetonitrile to give $Ni_3(dpa)_4(NCMe)_2(PF_6)_2$ with acetonitrile in the axial positions. Crystal data: triclinic; $a = 12.56(1)$ Å, $b = 12.802(9)$ Å, $c = 20.01(2)$ Å, $\alpha = 107.26(2)°$, $\beta = 98.83(3)°$, $\gamma = 101.54(5)°$, $V = 2932(4)$ Å^3; space group $P\bar{1}$; $Z = 2$. Berry, J. F.; Cotton, F. A.; Murillo, C. A. Unpublished results.

(27) $Cr_3(dpa)_4(BF_4)_2\cdot 2CH_2Cl_2$ crystal data: monoclinic; $a = 18.770(2)$ Å, $b = 17.003(2)$ Å, $c = 16.414(2)$ Å, $\beta = 111.768(2)°$, $V = 4864.9(8)$Å^3; space group *Cc*; $Z = 4$. Cr−Cr distances: 2.479(2), 2.052(2) Å. Berry, J. F.; Cotton, F. A.; Murillo, C. A. Unpublished results.

is unable to get close enough to the trinickel core since the equatorial F atoms would collide with the hydrogen atoms of the dipyridylamido ligands.

Compound **4** also contains a symmetric Cu_3 chain, but here the Cu···Cu distances of 2.51 Å are 0.04 Å longer than those in **3**. The structure retains the $M_3(dpa)_4Cl_2$ structural motif, with a $SbCl_6$ anion to balance the charge. The difference in Cu···Cu distances from **3** (2.47 Å) to **4** (2.51 Å) can be rationalized by assuming that, upon oxidation, an electron is removed formally from the central Cu atom with concurrent transformation of this atom to a d^8 square planar species. Evidence for this is seen in the Cu−N bond distances: those of the outer Cu−N bonds are of similar length to those in **3**, while the inner Cu−N bond distances of 1.88 Å are 0.09 Å shorter than those in **3**, signifying a greater attraction of the ligands to the more highly charged central Cu atom. Since the terminal Cu^{2+} ions see an increased charge on the central Cu^{3+} ion, they are electrostatically repelled, causing the Cu···Cu distances in **4** to be longer than those in **3**. This result provides a remarkable contrast to what happens upon oxidation of **1**. If the oxidation of **1** were mainly at the central Ni atom, an increase of the electrostatic repulsion between it and the two terminal Ni atoms would be expected along with a lengthening of the Ni···Ni distances. This, of course, is not what happens (the Ni−Ni distances both become 0.15 Å *shorter*), thus indicating that, instead of electrostatic repulsion between three positively charged metal ions, a significant attraction is present, which is consistent with 3c Ni−Ni bonding.

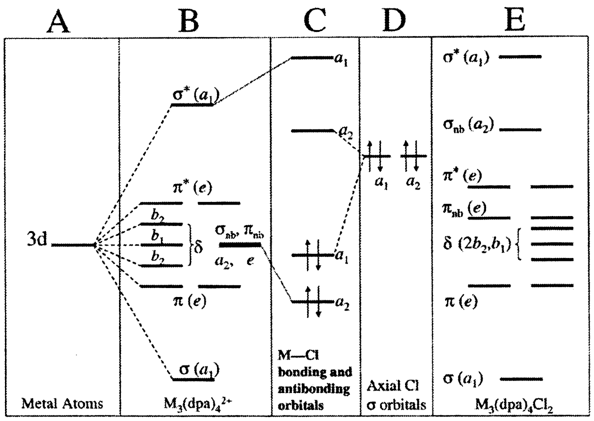
Discussion

Syntheses. While previously reported methods for the synthesis of **1** give fair yields, there are certain drawbacks to each. First, when using the Hurley and Robinson method, in which $Ni(Hdpa)_2Cl_2$ is heated to 285 °C in naphthalene and deprotonated by sodium butoxide in butanol,[13] all of the materials must be rigorously dry for the yield to be optimized. Also, this reaction utilizes 150 g of naphthalene as the solvent, which necessitates the use of larger glassware, high temperature, and removal of the product from a solid mass that makes the workup rather cumbersome.

The method of Clérac et al.,[3a] whereby anhydrous $NiCl_2$ is reacted with Lidpa, is more suitable to standard glassware and Schlenk techniques, but it is necessary to have extremely dry $NiCl_2$. Unfortunately, as is well-known, $NiCl_2$ is very hygroscopic (even deliquescent). Thus, for optimum results, the $NiCl_2$ must be refluxed in thionyl chloride and heated under dynamic vacuum immediately prior to use. It has been our experience that $NiCl_2$ which has been stored in a drybox for about a month after desiccation is again unsuitable.

In our preparation, $Ni(Hdpa)_2Cl_2$ is first prepared[13] and then deprotonated with methyllithium (eq 1). This starting material is not hygroscopic and is easily prepared, even on a scale of 10 g or more. Thus, the reaction is fully reproducible and consistent yields of 65% and higher are obtained. A minor drawback is that the reaction necessarily wastes some of the ligand, which is not easily recoverable, but is also not very expensive. It is also worth noting that $Ni(Hdpa)_2F_2$,[28] $Ni(Hdpa)_2Br_2$,[13] and $Ni(Hdpa)_2I_2$[13] are just as easily synthesized. This should make it possible in the future to prepare the complete set of trinickel dipyridylamido halides.

Scheme 2



$$3Ni(Hdpa)_2Cl_2 + 4MeLi \rightarrow Ni_3(dpa)_4Cl_2 + 4CH_4 + 4LiCl + 2Hdpa \quad (1)$$

Oxidation of **1** with $AgPF_6$ proceeds well at low temperature, but at room temperature solutions of **2** quickly decompose. Three equivalents of $AgPF_6$ are required to convert **1** to **2**, since silver reagents remove the axial chloride ions from the compound before they oxidize it (eq 2).

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

Compound **3** is easily synthesized[4a] in high yield from anhydrous $CuCl_2$ and Lidpa. Oxidation to **4** proved to be quite difficult. Though silver reagents easily oxidize **1** to **2**, the only reaction between **3** and $AgBF_4$ was the metathesis reaction resulting in $Cu_3(dpa)_4(BF_4)_2$ and AgCl even when $AgBF_4$ was in excess.[4a] Other strong and harsh oxidants such as nitrosonium reagents, diacetylferrocenium reagents, copper(II) triflate (in acetonitrile), and organic peroxides were used in attempts to oxidize **3**, but success was achieved only by using the powerful oxidant $[N(p\text{-}BrC_6H_4)_3][SbCl_6]$. This reaction was carried out in toluene, despite the insolubility of $[N(p\text{-}BrC_6H_4)_3][SbCl_6]$ in that solvent, but since **3** is quite soluble in toluene, the reaction occurs slowly, depositing **4** (eq 3). Excess **3** is removed by washing with toluene. Compound **4** is thermally unstable as a solid and in solution, and must be kept at low temperature (<0 °C).

$$Cu_3(dpa)_4Cl_2 + [N(C_6H_4Br)_3]SbCl_6 \rightarrow [Cu_3(dpa)_4Cl_2]SbCl_6 + N(C_6H_4Br)_3 \quad (3)$$

Electronic Structures. A generic diagram of the molecular orbitals that could form in a symmetrical $M_3(dpa)_4Cl_2$ molecule and a qualitative estimate of their relative energies is shown in Scheme 2. To obtain this diagram, we proceed in two steps:

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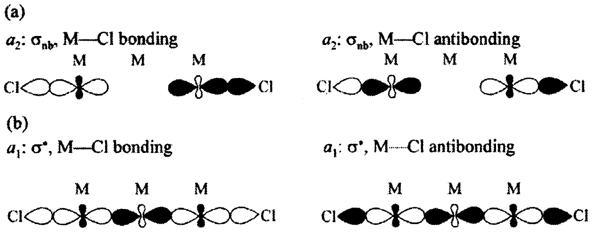
[28] Berry, J. F.; Cotton, F. A.; Murillo, C. A. Unpublished results.

Scheme 3



1. Advancing from column A to column B (Scheme 2), we first consider only the interaction of the three sets of metal d orbitals (d_{z^2}, d_{xz}, d_{yx}, and d_{xy}) with each other. Only interactions on adjacent metal atoms are considered large enough to matter, and, of course, symmetry considerations limit nonzero overlaps to only a few, namely, σ MOs formed from d_{z^2} orbitals, pairs of π orbitals formed from d_{xz} and d_{yz} orbitals, and δ MOs formed from d_{xy} orbitals.

The overlaps between d_{xy} orbitals are believed to be so small that δ, δ_{nb}, and δ^* orbitals will differ negligibly in energy. The π MOs will be significantly spread out and the σ MOs even more so. Thus, we arrive at the ordering shown in column B of the scheme for the $M_3(dpa)_4^{2+}$ portion of the molecule.

2. The interactions of the axial chlorine atoms with the trimetal chain are significant. The π interactions are probably less important than the σ interactions, and for present purposes we shall consider specifically only the latter.

In the D_4 point group the Cl^- lone pairs shown in column D form a symmetric and an antisymmetric set with a_1 and a_2 symmetry, respectively. The a_2 set is of the proper symmetry to interact with the σ_{nb} orbital of the trimetal unit causing the bonding and antibonding combinations to form as shown in Scheme 3a[29] and column C of Scheme 2. The a_1 combination of Cl^- σ orbitals can interact with both the a_1 σ orbital and the a_1 σ^* orbital of the trimetal chain. Here we assume that its interaction with the σ^* orbital is more important since the relative energy of Cl^- anions should be higher than that of the free M^{2+} cations (as shown in columns D and A, respectively).

Since the Cl^- orbitals in column D are filled, the lowest energy a_1 and a_2 orbitals in column C must be filled, and we can consider these as the M−Cl σ bonds. These two orbitals will not be considered further, since we are only concerned with the metal-based orbitals. The resulting orbital distribution is shown in column E. Figure 4 summarizes the ground states of the known $M_3(dpa)_4Cl_2$ molecules, and we will now briefly review the electronic structures of all of these compounds with reference to the formalisms presented in Scheme 2 and Figure 4.

$Cr_3(dpa)_4Cl_2^{n+}$ ($n = 0, 1$). Only symmetrical but not unsymmetrical trichromium compounds are expected to have the orbital pattern given in Scheme 2. Unsymmetrical compounds exist with a quadruple bond between two chromium atoms, and the third atom of the chain being five-coordinate and high spin ($S = 2$).[30] Symmetrical $Cr_3(dpa)_4Cl_2$ also has four unpaired electrons, however.[30] This is rationalized in Figure 4 by filling the σ and π bonding orbitals, and then the δ orbitals as well as the π_{nb} orbital, which are all nearly degenerate, this accounting for the four unpaired electrons.

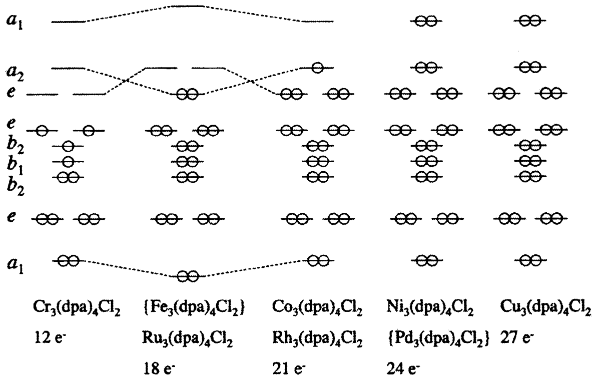


Figure 4. Qualitative molecular orbital scheme for $M_3(dpa)_4Cl_2$ compounds, M = Cr, Ru, Co, Rh, Ni, and Cu. For the limitation of this diagram for Ni_3^{6+} and $Cu_3^{6+/7+}$, see text.

Since all six known $Cr_3(dpa)_4Cl_2^+$ cations are unsymmetrical, they cannot be described by Scheme 2. Instead it is a localized system with a quadruply bound Cr_2 unit and a high-spin Cr^{3+} atom which gives the complex the observed $S = {}^3/_2$ ground state.[10]

$Ru_3(dpa)_4Cl_2$. If only Scheme 2 were considered for a Ru_3^{6+} unit, it may be expected that the symmetrical $Ru_3(dpa)_4Cl_2$ would have two unpaired electrons, since the 18 d electrons will fill the σ, π, δ, and π_{nb} orbitals leaving the last two electrons unpaired in the π^* orbital. The compound, however, is reported as being diamagnetic by S.-M. Peng et al.[5] At first glance, it would appear that the MO diagram in Scheme 2 is in error, since it does not fit the experimental facts. But, the Ru−Ru distances and Ru−Cl distances must also be considered here: $Ru_3(dpa)_4Cl_2$ has the shortest M−M distances (2.25 Å) and the longest M−Cl distances (2.60 Å) of all the symmetrical $M_3(dpa)_4Cl_2$ compounds. Thus, it may be anticipated that the M−M bonding orbitals will interact more strongly, pushing the σ and π bonding orbitals down in energy, and destabilizing the σ^* and π^* antibonding orbitals. Moreover, because of the very long M−Cl interactions, the σ_{nb} orbital (which has significant M−Cl antibonding character) should be lowered significantly in energy. This is shown in Figure 4 by reversing the order of these orbitals. Thus, filling the orbitals with the 18 d electrons accounts for the experimental singlet ground state.

The one-electron-oxidation product of this compound would be expected to have similar metal−metal distances, but the M−Cl distances will become shorter. Indeed this has been shown recently.[31]

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(29) Scheme 3 is meant to be only a schematic diagram that shows only the relative signs of the orbitals. No attempt has been made to quantify the ligand contributions to these orbitals. Thus, having all orbitals shown the same size is correct and appropriate. DFT calculations, however, have shown that σ_{nb} orbitals are approximately 70% metal based and ~25% Cl based (see ref 12).

(30) Clerac, R.; Cotton, F. A.; Daniels, L. M.; Dunbar, K. R.; Murillo, C. A.; Pascual, I. *Inorg. Chem.* **2000**, *39*, 748.

(31) Peng, S.-M. Private communication.

$Co_3(dpa)_4Cl_2^{n+}$ ($n = 0, 1$), $Rh_3(dpa)_4Cl_2$. Scheme 2 straightforwardly predicts an $S = {}^1/_2$ ground state for $Co_3(dpa)_4Cl_2$ and $Rh_3(dpa)_4Cl_2$, which agrees with the experimental observations.[2c,5] Theoretical work at the density functional level of theory on symmetrical $Co_3(dpa)_4Cl_2$ has shown indeed that the SOMO is σ_{nb} with antibonding Co–Cl interaction.[12] $Co_3(dpa)_4Cl_2$ does exist in an unsymmetrical form,[2b] but again we consider this a localized electronic structure which is neither predicted nor explained by Scheme 2.

The one-electron oxidation of $Co_3(dpa)_4Cl_2$ has been previously reported by us to give $Co_3(dpa)_4Cl_2^+$, which has a singlet ground state,[11] as predicted by the orbital scheme in Figure 6. The evidence for removal of a σ_{nb} M–Cl antibonding electron is seen by the changes in the Co–Co distances and the Co–Cl distances in the neutral molecule vs the cation in the oxidized species. Though the Co–Co distances do not change much (<0.01 Å), the Co–Cl distances are 0.15 Å shorter in $Co_3(dpa)_4Cl_2^+$. Scheme 2 also accounts for the unusual magnetic properties of $Co_3(dpa)_4Cl_2^+$, as has been previously noted.[11]

$Ni_3(dpa)_4Cl_2$ and $Ni_3(dpa)_4(PF_6)_3$. If a delocalized model of the electronic structure of $Ni_3(dpa)_4Cl_2$ is used, Figure 4 predicts the compound to be diamagnetic. This, however, is not the case: $Ni_3(dpa)_4Cl_2$ has four unpaired electrons.[3a] The right way to view the electronic structure of **1**, as has been pointed out before,[3a] is that the central nickel(II) atom is in a low-spin state because it is in a strongly tetragonal (roughly speaking, square) environment. Each of the two outer nickel(II) atoms has two unpaired electrons, and there is antiferromagnetic coupling between them that leads to a temperature-dependent magnetic moment. This formulation of the electronic structure leads to the conclusion that there is no net nickel–nickel bonding, consistent with the relatively long Ni···Ni separations of 2.43 Å.

When one electron is removed from the $Ni_3(dpa)_4Cl_2$ molecule, qualitative as well as quantitative changes occur in the molecular structure as well as the electronic structure. When the Ni–Ni distances become much shorter (changing from 2.43 to 2.28 Å), the Ni_3 chain becomes a delocalized system to which the molecular orbital formalism described above is applicable. In the $[Ni_3(dpa)_4(PF_6)_2]^+$ ion there is only one unpaired electron exactly as would be expected from the MO treatment. The EPR spectrum (Figure 5) shows an axial signal where $g_{||}$ appears to be split into a triplet by coupling to two axial fluorine nuclei belonging to the coordinated PF_6^- ions. Axial interactions in the $M_3(dpa)_4X_2$ compounds are generally strong, thus affecting the σ_{nb} and σ^* orbitals of the M_3 units as has just been discussed.

The electronic spectrum of **2** has also been recorded in solution and in the solid state, and it consists of two main peaks: one at 580 nm in the visible region and a less intense peak at 1045 nm in the near-IR. Though we have a qualitative idea of the ordering of the MO's in this compound, it is difficult to speculate as to the assignment of these peaks.

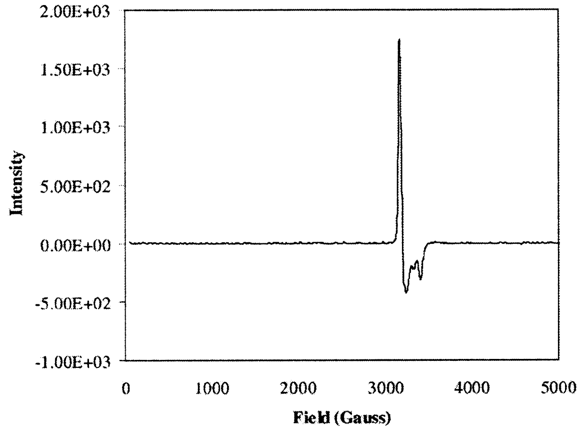

Figure 5. X-Band EPR spectrum of **2** taken in dichloromethane glass at 8 K.

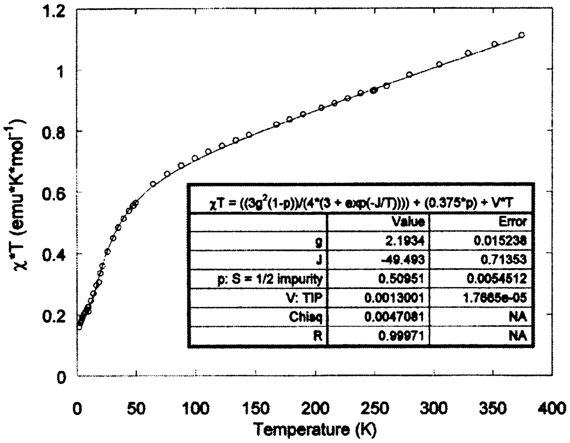

Figure 6. Plot of χT vs T for **4**. The solid line is the theoretical fit of the data. The equation given in the inset is a modification of the Bleaney–Bowers equation.

The change in **1** to **2** from a localized to a delocalized chain of metal atoms has some interesting implications. While the localized system is presumably not capable of efficient electron transfer along the metal chain, the delocalized system is likely to be a conductor. This would mean that a single molecule could serve as an on–off switch, controlled by an applied oxidation potential. The molecule can also serve as a physical switch, the length of the chain contracting from 4.88 to 4.57 Å upon applied potential. An aligned array of molecules could serve as a rheostat controlled either by an applied potential or in response to the concentration of molecules or ions capable of effecting the oxidation. In the event that the same kind of insulator–conductor conversion would occur for homologous molecules with longer metal chains,[6,7] the possibility of creating what are literally molecular wires (i.e., a central core of metal atoms aligned in a row surrounded by organic insulation) may be contemplated.

$Cu_3(dpa)_4Cl_2^{n+}$ ($n = 0, 1$). Turning now to the copper compounds, $Cu_3(dpa)_4Cl_2$ and $[Cu_3(dpa)_4Cl_2]SbCl_6$, we note that again there are two possible ways to look at their electronic structure: localized or delocalized. For the neutral molecule the localized picture would have three nonbonded copper(II) d^9 ions, whose spins might couple to give either a doublet or a quartet state. In view of the well-known behavior of dinuclear copper(II) compounds a doublet ground state would seem most likely,[32] and this has been shown to be the case.[4a] If a delocalized model is considered we note that of the 27 metal-based electrons available, 24 would fill the 12 MO's shown in Scheme 1, resulting in no net bonding. If the 4s orbitals also overlap sufficiently to form 3c MO's, we would perhaps assign two electrons to the bonding MO and one to a nonbonding MO based on the two outer Cu^{II} atoms. The experimental data cannot definitively distinguish between these two possibilities. The compound has a ground state with one unpaired electron (which is compatible with either formulation) and a quartet state that lies 560 cm^{-1} higher.[4a] From the structural point of view, the Cu···Cu distances (ca. 2.47 Å[4]) are also indecisive. Since there could be at most a bond order of $^1/_2$, based on net bonding via the 4s orbitals, this distance is short, compared to those typically found in binuclear copper(II) compounds such as the carboxylates (2.60 Å to well over 3 Å) although some dicopper tetrabenzamidinate compounds have Cu···Cu separations of ca. 2.46 Å.[33] Nevertheless, this cannot be said to show that either the outer three 4s electrons or the inner 24 electrons from the 3d are delocalized. It is simply indecisive. The energy difference between the ground doublet and excited quartet states, however, is indicative of there being antiferromagnetic coupling. This further supports the idea of the nonexistence of the Cu−Cu bond as shown by DFT calculations done using a $Cu_2(HNNNH)_4$ model.[34]

The electronic spectrum (vis, near-IR) of **4** in solution and in the solid consists of two broad bands. The first transition, at 487 nm, has been assigned tentatively to the central, square-coordinated Cu^{III} ion. The second, at 700 nm, may be assigned to the terminal Cu^{II} species. In solution, a band at 1310 nm appears which may be due to an intervalence charge transfer transition, in which an electron moves from a terminal Cu^{II} atom to the central Cu^{III} atom.[35]

The magnetic susceptibility data for compound **4** are shown in Figure 6. They are interpretable, but difficulties in handling the unstable compound have prevented the acquisition of data devoid of paramagnetic impurities. The data can be fit to the Bleaney−Bowers equation with parameters added to account for $S = {}^1/_2$ impurities or metallic impurities. The fitting shows that the compound contains two $S = {}^1/_2$ centers (presumably the terminal Cu^{II} ions) which are antiferromagnetically coupled with the exchange parameter $J = -34$ cm^{-1}.

Comparison with Other Ni^{III} and Cu^{III} Compounds. Complexes having Ni and Cu in formal oxidation states of +3 represent only a very small percentage of those known for these elements.[36] Nevertheless, great efforts have been devoted to their preparation and study as some evidence exists of possible participation in biological processes.[37] Early work on the stabilization of Ni^{III} [38] and Cu^{III} [39] by peptide ligands was done by Margerum's group in the 1970s and followed up in other laboratories.[40]

Complexes described as having Ni^{III} and porphyrin-like derivatives,[41] other N-ligands,[42] and thiolates[43] have been avidly sought also. Likewise, Schiff base ligands have been used to stabilize low-spin, square planar d^8 complexes of Cu^{III}.[44] Some controversy exists on whether some of the claims of M^{III} species are correct, particularly when non-innocent ligands are involved.[45]

More recently there has been great excitement due to the preparation of $M_2^{III}(\mu\text{-O})_2$ units for Ni[46] and Cu.[47] A singly oxo-bridged dinuclear Ni^{III} complex has been fully characterized also.[48] A complex relevant to our discussion of **2** is $Ni_2(DTolF)_4BF_4$ (where DTolF is the anion of *N*,*N*′-di-(*p*-tolyl)formamidine), which has a dinuclear Ni_2^{5+} unit.[49] This is obtained by a one-electron oxidation of $Ni_2(DTolF)_4$, and the chemistry is similar to the oxidation of **1** to **2** (vide supra). While there is no metal−metal bond in the latter, a bond order of 0.5 exists in the former.[49] The Ni−Ni distance in the unoxidized compound is 0.067 Å longer than that in the cation $Ni_2(DTolF)_4^+$, which is 2.418(4) Å.

Also relevant to **3** and **4** are compounds having a triangular $[Cu_3(\mu\text{-O})_2]^{3+}$ core. In $[Cu_3(\mu\text{-O})_2L_3](CF_3SO_3)_3$, L = *N*,*N*,*N*′,*N*′-tetramethyl-(1*R*,2*R*)-cyclohexanediamine, and the three copper atoms are bridged by the oxygen atoms and are four coordinate, but two of them display longer Cu−O distances of 1.95−2.01 Å while the corresponding distances to the third copper atom are only 1.84 Å. Thus, the latter has been assigned as the Cu^{III} atom and the core can be described as a localized, mixed-valence Cu(II,II,III) system having effective C_{2v} symmetry.[50] This localized structure resembles

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Table 6. Qualitative Description of M_3 Electron Density

compound	neutral	oxidized
$Cr_3(dpa)_4Cl_2$	localized or delocalized	localized
$Co_3(dpa)_4Cl_2$	localized or delocalized	delocalized
$Ni_3(dpa)_4Cl_2$	localized	delocalized
$Cu_3(dpa)_4Cl_2$	localized	localized

that of **4** where the central, square planar Cu atom is oxidized and it is flanked by two five-coordinate Cu^{II} ions (vide supra).

Another important system which is somewhat related to the work presented here is the family of linear trimetal compounds studied by Fackler's group.[51] They have found that $[Au_2Pt]^{4+}$ can be transformed to $[Au_2Pt]^{6+}$ by oxidative addition of substrates such as halogens,[52] giving products with Au−Pt−Au bonds. The $[Au_2Pb]^{4+}$ analogue, however, does not give oxidative addition products.[53] Thus, the reactivity of these compounds toward oxidants is based on the ease of M−M bond formation in the oxidized products. This is similar to the chemistry of **1** and **2**.

Conclusion. We have now completed our study of the one-electron-oxidation products of the four known $M_3(dpa)_4Cl_2$ compounds of the first-row transition metals. Table 6 summarizes our findings with respect to the nature of the electronic structure of these compounds. Localization and delocalization are loosely defined by the inapplicability or applicability of a three-center MO diagram as in Scheme 2 or Figure 4 in describing all of the physical data for each compound. Thus, the symmetrical $Cr_3(dpa)_4Cl_2$ can be described as a system with four unpaired electrons delocalized over the three metal atoms. The unsymmetrical $Cr_3(dpa)_4Cl_2$, however, with a short Cr−Cr quadruple bond, and no bond to the third Cr atom, has a localized structure: 8 electrons localized within the Cr−Cr quadruple bond, and four unpaired electrons on the isolated high-spin Cr^{2+} atom.[30] It appears to be only by chance that the two molecules exist in the same spin state. For $Co_3(dpa)_4Cl_2$, the case is similar. When the trichromium compounds are oxidized, the products are always unsymmetrical;[10] but oxidation of $Co_3(dpa)_4Cl_2$ gives a symmetrical compound with a singlet ground state.[11] In this work, we have shown that oxidation of the localized $Ni_3(dpa)_4Cl_2$ system gives a compound with delocalized three-center metal−metal bonds, and that oxidation of $Cu_3(dpa)_4Cl_2$ leads to a system which is still localized.

Here, we recognize that delocalization of electron density along a M_3 chain implies conductivity, and that delocalized $M_3(dpa)_4X_2$ systems can function as wires at a molecular scale. We are currently working on ways to test this idea, but it appears from the data gathered here that Cr_3, Co_3, or Ni_3 compounds may indeed function as molecular wires. Peng has shown that it is possible to prepare "wires" of this kind with longer M_n chains ($n = 4, 5, 7, 9$).[7] Based on our work with the M_3 compounds, we can see that the nickel chains must be "hole doped" (i.e., oxidized) in order to achieve molecule-scale conductivity. This is similar to what has been found for columns of stacked square planar Pt complexes.[54] Also, we have mentioned before[8] that junctions of Ni_n^{2n+} and $Ni_n^{(2n+1)+}$ can lead to molecule-scale diode-like behavior. The thermal instability of $Ni_3(dpa)_4^{3+}$ may hinder efforts to study this, but we also predicted that Ni_n with $n > 3$ would be more stable and more amenable to such a study. We are also focusing our research into the development of new ligands which will hold several metal atoms in a linear array which will be more robust toward oxidation and more useful in future applications as molecular devices.

At this point, there appears to be no good way to ensure that the Cr_3 or Co_3 chains are delocalized, since the factors which influence the metal−metal distances (symmetrical vs unsymmetrical structures) are apparently on the order of the energy differences between the different crystalline compounds. It can be expected, however, that the oxidized Cr_3 chains cannot be conducting, and that the oxidized Co_3 chain will be conducting. The Cu_3 chains show no specific indication of delocalization, even upon oxidation, and can perhaps further be used as an insulating standard by which to judge the success or failure of the other trimetal chains in conductivity experiments yet to be devised.

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Supporting Information Available: X-ray crystallographic data in CIF format for $\mathbf{1}\cdot Et_2O$, $\mathbf{1}\cdot$2toluene$\cdot$0.5hexane, $\mathbf{2}\cdot 5CH_2Cl_2$, $\mathbf{4}\cdot 2.86C_2H_4Cl_2\cdot 0.792C_6H_{12}$, and $\mathbf{4}\cdot 2.44C_3H_6O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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