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First Structural and Magnetic Studies of Ni Clusters Containing 2,6-Diacetylpyridine-dioxime as a Ligand

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In the present work, coordination possibilities of the system dapdoH$_2$/Ni^{2+}, being dapdoH$_2$ = 2,6-diacetylpyridine dioxime, have been explored, offering as a result a number of unprecedented clusters with a variety of topologies and magnetic behaviors. Depending on the precursors and reaction conditions, several compounds named [Ni$_2$(dapdo)$_2$] (**1**), [Ni$_3$(OH)(BzO)$_3$(dapdo)(dapdoH$_2$)(H$_2$O)]·1.25H$_2$O (**2**), [Ni$_3$(AcO)$_4$(dapdoH)$_2$(H$_2$O)$_2$]·H$_2$O (**3**), and [Ni$_4$(AcO)$_3$(dapdo)(dapdoH)$_2$(H$_2$O)$_3$]·(AcO)·3H$_2$O (**4**) were achieved and structurally well-characterized. Dc magnetic measurements were carried out in the 2−300 K range revealing antiferromagnetic interactions for (**2**−**4**) compounds and diamagnetic response for the square planar coordinated complex (**1**).

Introduction

At present, research of oximes in coordination chemistry is a growing field. 2-pyridyl oximes are well-known ligands in this area because of their ability to generate stable first-row transition coordination compounds with a large range of nuclearities.[1] These molecules are very versatile, able to act as bidentate ligands in their neutral state or to link up to three metallic centers in their deprotonated anionic form. Self-assembly of metal-oximato fragments have yielded a large amount of high nuclearity clusters, as for example: Ni$_7$,[2] Ni$_9$,[3] Ni$_{10}$,[4] Ni$_{12}$ or Ni$_{14}$,[5] Fe$_{12}$,[6] and Mn$_8$,[7] Mn$_9$,[8] Mn$_{10}$,[9] and Mn$_{12}$,[10] exhibiting in some cases SMM response.[7,10]

One of the crucial synthetic points in the search of high nuclearity systems is the design of ligands to increase such nuclearity and/or generate new topologies. Regarding this matter, pyridyl dioximato ligands (LH$_2$, with R = various), Scheme 1, appear as excellent candidates for the achievement of polynuclear clusters in the bottom-up approach: they contain a good N-donor unit (pyridinic ring) and two meta-oximato groups capable of binding four metal centers, M in Scheme 2.

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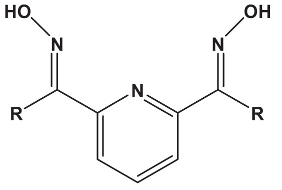
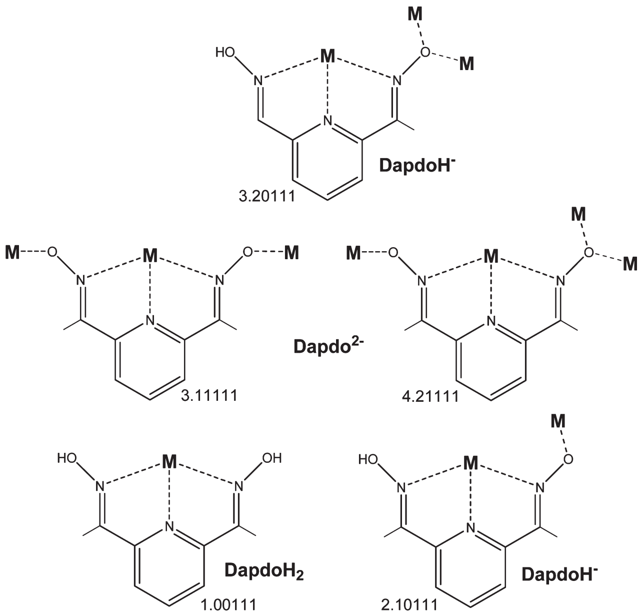
Scheme 1. LH_2 Dioxime Ligands (R = H, Me, NH_2); DapdoH_2 Refers to the Ligand in Which R = Me



Scheme 2. Coordination Modes for dapdoH_2, dapdoH^-, or dapdo^{2-} Ligands[a]



[a] A large number of unprecedented possibilities as the novel coordination mode 3.20111 reported in this work for dapdoH^- are still possible.

Within this family of linkers, 2,6-diacetylpyridine dioxime (dapdoH_2) is the most well-studied and only a few examples using related ligands like 2,6-pyridine dioxime (pdoH_2) or pyridine-2,6-diamidoxime (pdamoH_2) have been reported to date.[1]

On the other hand, the putative capacity of dapdoH_2 for the development of high nuclearity systems differs from current results in the literature, where the majority of compounds happen to be mononuclear. Thus, a number of systems with general formula $[M^{II}(LH_2)_2]X_2$ (M = Cu,[11] Ni,[12] Fe,[13] Mn[11a]), including one $[Ni^{II}(pdamoH)_2]$[14] and two $[M^{IV}(dapdo)_2]$ (M^{IV} = Ni,[15] Co[16]) have been described. In all of them, the six coordination sites of the metallic centers are shielded by two LH_2, LH^-, or L^{2-} ligands in 1.00111 coordination modes (Harris notation),[17] respectively. In addition, several mononuclear complexes containing one dapdoH_2 ligand in the 1.00111 coordination mode along with anions or solvent molecules linked in the remainder positions of the coordination sphere of metal have been found with Cu^{2+},[18] Zn^{2+},[18a] In^{3+},[19] and Ru^{2+}.[20] Besides, some of these coordinated anions may also bind neighboring centers giving as a result 1D systems in which dapdoH_2 acts exclusively as a tridentate ligand (e.g., $[Cu(pdamoH_2)(\mu\text{-}SO_4)]_n$[12] and $[Mn(dapdoH_2)(\mu\text{-}Cl)_2]_n$).[21] Recent reports show similar coordination properties for certain trinuclear systems, $[Mn_3(dapdoH_2)_2(R\text{-}COO)_6]$ (R = H, Me, Ph).[22]

Nevertheless, it should be emphasized the existence of some polynuclear clusters generated after deprotonation of dapdoH_2; where now, the resulting anionic species (dapdoH^- and/or dapdo^{2-}) play a primary role. This group of compounds comprises a dinuclear copper system that contains a double oximato bridge and two dapdoH^- ligands in 2.10111 coordination modes, which general formula is $[Cu_2(dapdoH)_2](BF_4)_2$;[23] a mixed valence trinuclear Fe system in which one $\{Fe^{II}(dapdoH)_2\}$ subunit is linked to two Fe^{3+} cations, described as $[Fe^{II}(dapdoH)_2Fe^{III}Cl_4(O)]$;[13] an heterometallic copper−chromium compound in which {Cu(dapdo)} subunits bind chromium triazacyclononane groups in a 3.11111 coordination mode;[24] a family of $Mn^{II}_2Mn^{III}_4$ hexanuclear anionic species expressed as $[Mn_6O_2(MeO)_2(dapdo)_2(dapdoH)_4]^{2+}$;[25] a mixed valence $[Mn^{II}_2Mn^{III}_6O_4(OH)_4(MeO)_2(N_3)_2(dapdo)_2(dapdoH)_2(H_2O)]$[25a] complex and finally an heterometallic Mn/Gd trinuclear system.[26]

Here, we introduce the first polynuclear clusters achieved by reacting dapdoH_2 with different nickel salts in basic conditions. This approach has led to the formation of unique structures, Ni_2 (**1**), Ni_3 (**2**, **3**), and Ni_4 (**4**), that include the organic unit or its deprotonated forms exhibiting a variety of coordination modes. Syntheses, structures, and magnetic behaviors of these compounds are described in the following sections.

Experimental Section

Syntheses. 2,6-Diacetylpyridine, $Ni(AcO)_2 \cdot 4H_2O$ and $Ni(acac)_2$ (acac = acetylacetonate) were purchased from Sigma-Aldrich Inc. and Flucka AG and used without further purification. $Ni(BzO)_2 \cdot 3H_2O$ was synthesized dissolving equimolar quantities (40 mmol) of benzoic acid and NaOH in 40 mL of

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H_2O, filtering and mixing the final solution with a commercial source of $Ni(NO_3)_2 \cdot 6H_2O$ (20 mmol) in 20 mL of water. The resulting nickel salt was obtained in good yield (>80%). DapdoH_2 was prepared following C.W. Glynn and M.M. Turnbull method.[11a]

[Ni_2(dapdo)$_2$] (1). DapdoH_2 (0.193 g, 1 mmol) and Ni(acac)$_2$ (0.514 g, 2 mmol) were dissolved in 20 mL of MeOH together with NEt_3 (0.202 g, 2 mmol). The mixture was stirred for 2 h and then filtered. Crystals were obtained by layering the final solution with 10 mL of diethyl ether. Anal. Calcd for $C_{18}H_{18}N_6Ni_2O_4$ (**1**): C, 43.26; H, 3.63, N, 16.82%. Found: C, 43.1; H, 3.7, N, 16.6%. Relevant IR bands (cm^{-1}): 3421(b), 1559(w), 1512 (w), 1399(s), 1299(m), 1273(m), 1196(s), 1151(m), 1118(m), 1087(s), 788(m), 559(m).

[Ni_3(OH)(BzO)$_3$(dapdo)(dapdoH_2)(H_2O)]$\cdot$1.25H_2O (2). DapdoH_2 (0.194 g, 1.0 mmol) and $Ni(BzO)_2 \cdot 3H_2O$ (0.602 g, 2 mmol) were dissolved in 40 mL of distilled MeOH and then NEt_3 (0.202 g, 2 mmol) was added. The solution was stirred for 2 h, filtered and crystallized layering with diethyl ether. Anal. Calcd for $C_{39}H_{38}N_6Ni_3O_{12} \cdot 1.25\ H_2O$ (**2**): C, 47.73; H, 4.16, N, 8.56%. Found: C, 47.8; H, 4.0, N, 8.8%. Relevant IR bands (cm^{-1}): 3436(b), 1599(s), 1340(s), 1214(w), 1121(w), 1087(w), 1044(w), 802(w), 721(m).

[Ni_3(AcO)$_4$(dapdoH)$_2$(H_2O)$_2$]$\cdot H_2O$ (3). A slurry of dapdoH_2 (0.193 g, 1 mmol) was dissolved in 20 mL of distilled MeOH and NEt_3 (0.202 g, 2 mmol) together with $Ni(AcO)_2 \cdot 4H_2O$ (0.494 g, 2 mmol). The solution was stirred for a couple of hours, filtered and crystallized layering with diethyl ether. Anal. Calcd for $C_{26}H_{36}N_6Ni_3O_{14} \cdot H_2O$ (**3**): C, 36.70; H, 4.50, N, 9.88%. Found: C, 35.3; H, 4.6, N, 9.5%. Relevant IR bands (cm^{-1}): 3400(b), 1577(s), 1410(s), 1213(m), 1167(m), 1058(m), 809 (m), 661(m).

[Ni_4(AcO)$_3$(dapdo)(dapdoH)$_2$(H_2O)$_3$](AcO)$\cdot$3H_2O (4). DapdoH_2 (0.193 g, 1 mmol) and $Ni(AcO)_2 \cdot 4H_2O$ (0.494 g, 2 mmol) were added to 20 mL of CH_2Cl_2 together with NEt_3 (0.202 g, 2 mmol). The solution was stirred and after a couple of hours, filtered and layered using hexane. Anal. Calcd for $C_{35}H_{47}N_9Ni_4O_{17} \cdot 3H_2O$ (**4**); C, 36.41; H, 4.63, N, 10.92%. Found: C, 35.2; H, 4.8, N, 10.5%. Relevant IR bands (cm^{-1}): 3396(b), 1572(s), 1517 (m), 1489(m), 1193 (m), 1167 (m), 1085 (m), 1060 (m), 811 (w), 715 (w), 669 (w).

Physical Measurements. Magnetic susceptibility measurements were carried out on polycrystalline samples with a DSM5 Quantum Design susceptometer working in the range 30−300 K under magnetic fields of 0.3 T and under a field of 0.03T in the 30−2 K range to avoid saturation effects. Diamagnetic corrections were estimated from Pascal Tables. Infrared spectra (4000−400 cm^{-1}) were recorded from KBr pellets on a Bruker IFS-125 FT-IR spectrophotometer.

X-ray Crystallography. Data for compound **1** were collected on a red block using a single-axis HUBER diffractometer on station BM16 of the European Synchrotron Radiation Facility, Grenoble, France. Cell refinement, data reduction and absorption corrections were done with HKL-2000 suite.[27] The structure was solved by direct methods and the refinement and all further calculations were carried out using SHELX-TL suite.[28] All non-hydrogens were refined anisotropically. Hydrogens were found in difference Fourier maps, placed geometrically on their riding atom and refined with a riding model.

Data for compound **2** were collected on an orange plate on a Bruker APEX II CCD diffractometer on Advanced Light Source beamline 11.3.1 at Lawrence Berkeley National Laboratory, from a silicon 111 monochromator . The structure was solved by direct methods and refined on F^2.[28] The crystal was found to be twinned, although attempts at finding a twinning matrix were unsuccessful. Twinning was thus taken into account with TWIN/BASF instructions in shelxl. All non-hydrogens were refined anisotropically, although displacement parameters restrains were used for a number of carbon atoms and the lattice water oxygens. Hydroxyl hydrogens were found in difference Fourier maps and refined with distance restrains. The rest of hydrogens were placed geometrically on their riding atom. At the end of the refinement, large voids remained in the structure containing only diffuse electron density that could not be modeled satisfactorily. These voids were thus analyzed and taken into account by PLATON/SQUEEZE,[29] that recovered a total of 276 electrons per cell in voids occupying a total of 1476 cubic angstroms (main voids volumes are 200 and 125 Å^3), resulting in a significant improvement both in R_1 and wR_2 factors. The derived figures (electrons/volume) would reasonably account for a number of diffuse small solvent molecules, e.g. water or methanol.

A red prismatic crystal of (**3**) was selected and mounted on a MAR345 diffractometer with an image plate detector. Unit-cell parameters were determined from 6640 reflections ($3 < \theta < 31°$) and refined by least-squares method. Lorentz-polarization and absorption corrections were made.

The structure was solved by direct methods, using SHELXS computer program[30] and refined by full-matrix least-squares method with SHELX97 computer program.[31] All H atoms were computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 time the equivalent temperature factor of the atom which are linked.

(**4**) Data collection of the data was made on a APEX2 (BRUKER AXS, 2005) diffractometer. Unit-cell parameters were determined from 1896 reflections ($2.3 < \theta < 23.4°$) and refined by least-squares method. The structure was solved using SIR97[32] and refined with SHELX97.[31]

Unit-cell parameters, structure, and refinement data are listed in Table 1.

Plots for publication were generated with ORTEP3 for Windows and plotted with Pov-Ray programs.[33]

Results and Discussion

Syntheses. There are several resemblances in the synthetic preparation of compounds **1**−**4**; however, the chemistry behind suggests a more complex picture than one may anticipate. This way, it was found that reactions using Ni(acac)$_2$ or Ni(tfacac)$_2$ (tfacac = trifluoroacetylacetonato) together with dapdoH_2 always yielded compound **1**, even if different reagent ratios, pH, or solvents were used. Basically, no examples of octahedral Ni compounds were achieved using acac or derivative ligands as starting materials. In contrast, compounds **2**−**4** could be easily obtained with $Ni(BzO)_2$ or $Ni(AcO)_2$ salts, correspondingly. Nevertheless, we may stress that all three complexes exhibit great dependency on other reactions variables. Hence, compound **2** was obtained using MeOH or 96% EtOH as solvents, and a small amount of H_2O in solution was mandatory. No compounds were isolated using dry solvents. Also, of particular interest it is the necessity of H_2O molecules that do not react or

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Table 1. Crystal Data and Structure Refinement for Compounds **1**−**4**

	(1)	**(2)**	**(3)**	**(4)**
formula	$C_{18}H_{18}$ $N_6Ni_2O_4$	$C_{156}H_{154}$ $N_{24}Ni_{12}O_{53}$	$C_{26}H_{38}$ $N_6Ni_3O_{16}$	$C_{35}H_{53}$ $N_9Ni_4O_{20}$
FW	499.76	3917.55	846.72	1154.63
space group	P21/c	P212121	Pca21	*C*2/*c*
a (Å)	8.319(2)	13.1697(9)	13.663(6)	17.9677(6)
b (Å)	14.755(3)	29.501(2)	14.994(4)	17.4069(7)
c (Å)	7.123(2)	44.867(3)	18.343(6)	35.032(1)
α (deg)	90	90	90	90
ss (deg)	92.28(3)	90	90	95.115(2)
γ (deg)	90	90	90	90
V (Å^3)	873.6(4)	17432(2)	3758(2)	10912.9(7)
Z	2	4	4	8
T (K)	150	150	293(2)	100
λ(MoK$_\alpha$) (Å)	0.75150	0.77490	0.71073	0.71070
ρ_{calcd} (g cm^{-3})	1.900	1.489		1.407
μ(MoK$_\alpha$), mm^{-1}	2.780	1.355	1.558	1.433
R	0.0344	0.0661	0.0746	0.0496
ωR^2	0.0958	0.1537	0.2076	0.1299

deprotonated, but complete the octahedral coordination of some of the metal ions of the clusters (**2**−**4**). Even more, intramolecular hydrogen bonds between water molecules among each other or with the rest of ligands in the structure are responsible for the closure and stability of the final compounds (see structural section). The nature of the solvent is critical too, becoming evident if one compares compounds **3** and **4**. These two complexes were obtained using identical reagents and ratios. However, compound **3** was accomplished using a polar solvent, MeOH, with some drops of H_2O, whereas reactions in CH_2Cl_2 led always to big crystals of compound **4**.

Finally, experiments using sodium azide together with H_2dapdo were carried out in a further attempt to achieve advance architectures. In contrast, the presence of azido anions in solution under aerobic conditions gave systematically dark crystals of the already reported mononuclear Ni(IV) complex containing two deprotonated dapdo^{2-} ligands, [Ni(dapdo)$_2$].[15]

In this sense, it is remarkable the coordination behavior of the deprotonated form dapdo^{2-} bonded to Ni^{2+} atoms. Ni^{IV} complexes derived from oximato anions are well-known (e.g., [Ni(dapdo)$_2$] and [Ni(dmg)$_3$]$^{2-}$, where dmg^{2-} stands for dimetylglioximato) and the stabilization of their high oxidation state has been related to strong spherical crystal fields, provided by the oximato groups themselves.[34] However, complexes **2**−**4** indicate that coordination of only one dapdo^{2-} ligand is not enough to favor the oxidation of Ni^{2+} to Ni^{4+} while always stabilizing the square planar environment around the metallic centers.

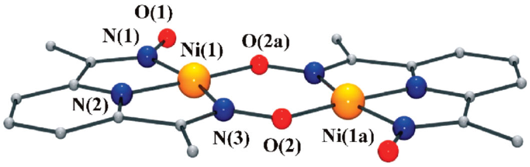

Figure 1. Labeled Pov-Ray plot of complex **1**. H atoms omitted for clarity.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for Vompound **1**

Ni(1)−N(1)	1.912(2)	Ni(1)−N(3)	1.927(2)
Ni(1)−N(2)	1.817(2)	Ni(1)−O(2a)	1.832(1)
N(1)−O(1)	1.282(2)	N(3)−O(2)	1.339(2)
N(1)−Ni(1)−N(2)	82.47(7)	N(3)−Ni(1)−O(2a)	104.84(7)
N(1)−Ni(1)−N(3)	164.58(7)	Ni(1)−N(1)−O(1)	124.4(1)
N(1)−Ni(1)−O(2a)	90.58(7)	Ni(1)−N(3)−O(2)	129.6(1)
N(2)−Ni(1)−N(3)	82.12(7)	Ni(1a)−O(2)−N(3)	125.5(1)
N(2)−Ni(1)−O(2a)	173.02(7)		

Description of the Structures. $[Ni_2(dapdo)_2]$ (1). A labeled plot of the neutral centrosymmetric dinuclear units present in compound **1** is shown in Figure 1. Selected bond parameters are listed in Table 2. The dinuclear units consist of two nickel atoms linked by two oximato bridges from two 2.10111 dapdo^{2-} ligands. Each nickel atom (Ni^{2+}, d^8), is coordinated by three N atoms from one of the dapdo^{2-} ligands and one O-oximato atom from the second dapdo^{2-} ligand, providing a distorted square planar environment. Bond distances lies in the 1.972(2)−1.817(2) Å range and the bond angles around the nickel atoms deviates from 90° due to the low bit angle of the dapdo^{2-} ligand, being N(1)−Ni(1)−N(2) and N(2)−Ni(1)−N(3) (82.47(7)° and 82.12(7)°, respectively), lower than the bond angles involving the oxygen atom O(2a)−Ni1−N(1) and O(2a)−Ni1−N(3) (90.58(7) and 104.84(7)°, respectively).

Both dapdo^{2-} ligands are totally deprotonated and surprisingly, the noncoordinated oximato groups are neither involved in coordination nor hydrogen bonding. The molecule is practically planar with a slight distortion in the Ni(1)−N(3)−O(2)−Ni(1a) torsion angle of 1.9(2)°. A single weak intermolecular interaction is observed corresponding to a $\pi-\pi$ stacking of the pyridinic rings of neighboring molecules, with a distance between centroids of 3.721 Å.

$[Ni_3(OH)(BzO)_3(dapdo)(dapdoH_2)(H_2O)]\cdot 1.25H_2O$ (2). The asymmetric unit of compound **2** contains four nonequivalent trinuclear units with similar core and bond parameters. A labeled plot of one of these neutral trinuclear units is shown in Figure 2. Selected bond parameters for this unit are also listed in Table 3. This trinuclear compound combines one tetracoordinated nickel atom Ni(2), in a distorted square-planar geometry, with two hexacoordinated nickel atoms, Ni(1) and Ni(3), connected together by a central μ_3−OH group. Coordination sphere of Ni(2) is formed by the three N-atoms from a 3.11111 dapdo^{2-} ligand and the central hydroxo ligand. Each oximato group of this deprotonated dapdo^{2-} links a second Ni^{2+} ion giving Ni(2)−N(5)−(O4)−Ni(1)

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(34) Baucom, E. I.; Drago, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 6469.

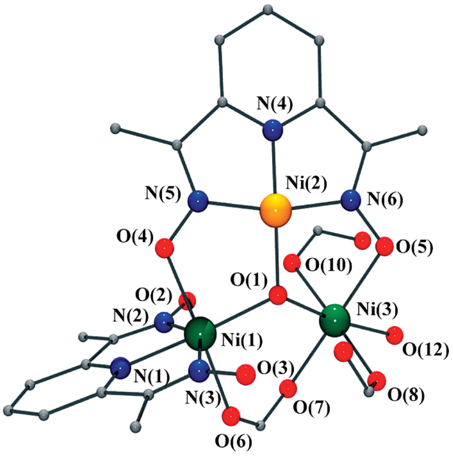

Figure 2. Labeled Pov-Ray plot of complex **2**. Ni atoms in octahedral or square planar environment are plotted in green and orange color in that order. Aromatic rings of the benzoate ligands and protons other than the NOH groups are omitted for clarity.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for Compound **2**

Ni(1)−N(1)	1.993(6)	Ni(1)−O(1)	2.001(5)
Ni(1)−N(2)	2.141(6)	Ni(1)−O(4)	2.091(5)
Ni(1)−N(3)	2.184(5)	Ni(1)−O(6)	2.042(5)
Ni(2)−N(4)	1.779(6)	Ni(2)−N(6)	1.862(6)
Ni(2)−N(5)	1.868(6)	Ni(2)−O(1)	1.859(5)
Ni(3)−O(1)	2.064(5)	Ni(3)−O(8)	2.043(4)
Ni(3)−O(5)	2.111(5)	Ni(3)−O(10)	2.108(4)
Ni(3)−O(7)	2.037(5)	Ni(3)−O(12)	2.099(5)
N(2)−O(2)	1.391(7)	N(3)−O(3)	1.394(8)
N(5)−O(4)	1.320(7)	N(6)−O(5)	1.319(8)
Ni(1)−O(4)−N(5)	114.0(4)	Ni(2)−N(5)−O(4)	122.7(4)
Ni(3)−O(5)−N(6)	108.7(4)	Ni(2)−N(6)−O(5)	122.0(4)
Ni(1)−O(1)−Ni(2)	113.7(2)		
Ni(1)−O(1)−Ni(3)	123.6(2)		
Ni(2)−O(1)−Ni(3)	105.4(2)		

and Ni(2)−N(6)−(O5)−Ni(3) bridges with torsion angles of 15.5 and 27.1°, respectively.

The core of **2** is highly asymmetrical, because of the two hexacoordinated Ni^{2+} atoms organize differently: coordination sphere of Ni(1) is completed with three N-atoms from one 1.00111 $dapdoH_2$ and one O-atom from one syn−syn benzoate ligand (with a Ni(1)−O(6)···O(7)−Ni(3) torsion angle of 46.8°); meanwhile, Ni(3) coordinates two additional monocoordinated benzoate groups and completes the octahedral environment with a molecule of water. N−M−N bond angles for $dapdo^{2-}$ and $dapdoH_2$ ligands are strongly modified by deprotonation and O-coordination: N(4)−Ni(2)−N(5) and N(4)−Ni(2)−N(6) (83.4(3) and 83.4(3)°, respectively) are considerably higher than N(1)−Ni(1)−N(2) and N(1)−Ni(1)−N(3) (76.1(2) and 76.3(2)°, in that order). Bond angles involving the hydroxo ligand are also highly asymmetric: (Ni(1)−O(1)−Ni(2), Ni(2)−O(1)−Ni(3) Ni(1)−O(1)−Ni(3) bond angles are 113.7(2), 105.4(2), and 123.6(2)°) giving an irregular triangle which distances: Ni(1)···Ni(2), Ni(2)···Ni(3), and Ni(1)···Ni(3) are 3.232, 3.124, and 3.583, respectively. Overall, Ni−N distances lie in a 1.779(6)−1.868(6) Å range for $dapdo^{2-}$, whereas they remain between 1.993(5) and 2.184(5) Å in the case of $dapdoH_2$. Ni−O distances lies in a shorter range comprised between 2.001 and 2.111 Å.

The orientation and distance between the centroids of the pyridinic ring of $dapdo^{2-}$ and the benzylic ring of one of the terminal benzoates, > 3.90 Å, may be pointed as weak π−π stacking.

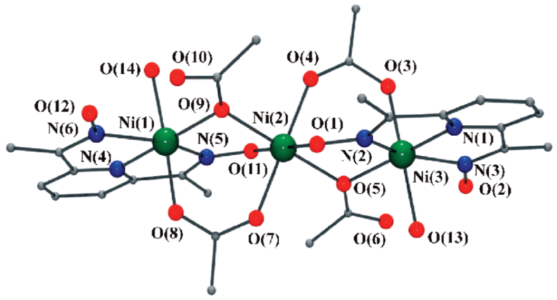

Figure 3. Labeled Pov-Ray plot of complex **3**.

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for Compound **3**

Ni(1)−N(4)	1.996(8)	Ni(1)−O(8)	2.053(6)
Ni(1)−N(5)	2.056(8)	Ni(1)−O(9)	2.058(6)
Ni(1)−N(6)	2.201(8)	Ni(1)−O(14)	2.127(6)
Ni(2)−O(1)	2.075(6)	Ni(2)−O(7)	2.087(6)
Ni(2)−O(4)	2.084(6)	Ni(2)−O(9)	2.182(6)
Ni(2)−O(5)	2.159(6)	Ni(2)−O(11)	2.075(6)
Ni(3)−N(1)	1.998(8)	Ni(3)−O(3)	2.017(6)
Ni(3)−N(2)	2.004(8)	Ni(3)−O(5)	2.061(6)
Ni(3)−N(3)	2.197(9)	Ni(3)−O(13)	2.152(6)
N(2)−O(1)	1.335(10)	N(3)−O(2)	1.362(13)
N(5)−O(11)	1.295(11)	N(6)−O(12)	1.316(11)
Ni(1)−N(5)−O(11)	124.8(5)	Ni(2)−O(11)−N(5)	112.3(4)
Ni(3)−N(2)−O(1)	126.1(5)	Ni(2)−O(1)−N(2)	111.5(4)
Ni(1)−O(9)−Ni(2)	103.5(3)	Ni(2)−O(5)−Ni(3)	105.1(3)

$Ni_3(AcO)_4(dapdoH)_2(H_2O)_2]\cdot H_2O$ (3). A labeled plot of the neutral trinuclear unit of **3** is depicted in Figure 3 and selected bond parameters are listed in Table 4. This linear compound contains three hexacoordinated nickel atoms, bounded to a total of two 2.10111 $dapdoH^-$ molecules, four bridging acetate anions, and two water molecules.

$DapdoH^-$ molecules act as terminal ligands, capping terminal Ni(1) and Ni(3) centers by binding them through their three nitrogen atoms, respectively. The central nickel atom is coordinated to one deprotonated O-oximato of each $dapdoH^-$. At the same time, two bridging acetate anions, in η^1,μ-AcO and η^2,μ-AcO modes, connect Ni(2) with each Ni(1) and Ni(3) metallic centers. Finally, there are two water molecules that complete the coordination sphere of Ni(1) and Ni(3), respectively. Four Ni−N distances close to 2 Å corresponds to the bonds with the pyridinic rings (N(4)−Ni(1) and N(1)−Ni(3)) and the deprotonated oximato group (N(5)−Ni(1) and N(2)−Ni(3)) whereas two larger bond distances close to 2.2 Å involve the links with the protonated oxime groups (N(6)−Ni(1) and N(3)−Ni(3)). Ni−O distances range between 2.017 and 2.182 Å. N−Ni−N bond angles ranged between 74.7 and 80.8° because of the low bite of the $dapdoH^-$ ligands. At last, N−O−Ni angles are 112.1(4)° for N(5)−O(11)−Ni(2) and 111.77(4)° for N(2)−O(1)−Ni(2). The molecule deviates from planarity, with the Ni(1)−N(5)−O(11)−Ni(2) and Ni(3)−N(2)−O(1)-Ni(2) torsion angles being slightly greater than 20°.

$[Ni_4(AcO)_3(dapdo)(dapdoH)_2(H_2O)_3](AcO)\cdot 3H_2O$ (4). Figure 4 shows the labeled plot of the cationic tetranuclear structure of this compound. Selected bond parameters are listed in Table 5. The core of **4** consists of one

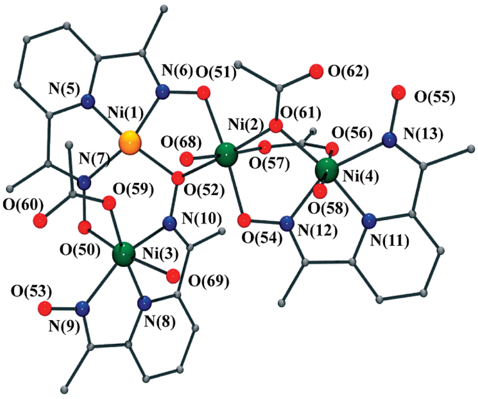

Figure 4. Labeled Pov-Ray plot of complex **4**. Ni atoms in octahedral and square planar environments are plotted in green and orange colors, respectively.

Table 5. Selected Interatomic Distances (Å) and Angles (deg) for Compound **4**

Ni(1)−N(5)	1.819(3)	Ni(1)−N(7)	1.931(3)
Ni(1)−N(6)	1.885(3)	Ni(1)−O(52)	1.869(3)
Ni(2)−O(51)	2.023(3)	Ni(2)−O(57)	2.052(3)
Ni(2)−O(52)	2.115(3)	Ni(2)−O(61)	2.088(3)
Ni(2)−O(54)	2.012(3)	Ni(2)−O(68)	2.052(3)
Ni(3)−N(8)	1.984(3)	Ni(3)−O(50)	2.069(3)
Ni(3)−N(9)	2.085(3)	Ni(3)−O(59)	2.018(3)
Ni(3)−N(10)	2.048(3)	Ni(3)−O(69)	2.144(3)
Ni(4)−N(11)	1.985(4)	Ni(4)−O(56)	2.044(3)
Ni(4)−N(12)	2.038(3)	Ni(4)−O(58)	2.110(3)
Ni(4)−N(13)	2.117(4)	Ni(4)−O(61)	2.045(3)
N(6)−O(51)	1.314(4)	N(7)−O(50)	1.348(4)
N(9)−O(53)	1.367(4)	N(10)−O(52)	1.387(4)
N(12)−O(54)	1.333(4)	N(13)−O(55)	1.394(6)
Ni(1)−N(6)−O(51)	124.3(2)	Ni(2)−O(51)−N(6)	114.2(2)
Ni(1)−N(7)−O(50)	127.9(2)	Ni(3)−O(50)−N(7)	110.2(2)
Ni(3)−N(10)−O(52)	124.9(2)	Ni(1)−O(52)−N(10)	113.2(2)
		Ni(2)−O(52)−N(10)	115.9(2)
Ni(2)−O(54)−N(12)	110.6(2)	Ni(4)−N(12)−O(54)	124.3(2)
Ni(1)−O(52)−Ni(2)	110.3(1)	Ni(2)−O(61)−Ni(4)	104.2(1)

tetracoordinated nickel atom, Ni(1), and three hexacoordinated nickel centers, Ni(2)−Ni(4). Ni(1) environment consist of three N-atoms from one 3.11111 dapdo^{2-} ligand and one O-oximate bridging atom from one exhibiting a distorted square-planar geometry. The deprotonated oximato groups connect Ni(1) with Ni(2) and Ni(3) in a similar fashion of Ni(2) in complex **3**. Ni(3) is bounded to the three N-atoms of one dapdoH^{-} ligand that displays the novel 3.20111 coordination mode (unprecedented until now), one bridging O-oximato atom, one monocoordinated acetate group, and one water molecule, giving octahedral environment. This dapdoH^{-} ligand assist as a link among Ni(1), Ni(2) and Ni(3). A second dapdoH^{-} ligand exhibiting a 2.10111 coordination mode, is found to be coordinated to Ni(4) by their three N-atoms. Again, the deprotonated O-oximato attaches Ni(2) and Ni(4) and the octahedral environment of both metals is completed by the coordination of two AcO^{-} ligands in a η^1,μ-AcO and η^2,μ-AcO way and two molecules of water, correspondingly.

Ni−N and Ni−O distances lie in the 1.819−2.144 Å range, where the shortest correspond to the square planar Ni(1). As it was found in previous compounds, N−Ni−N angles are clearly lower than 90° lying between 75.3−82.4°, corresponding to the largest observed with deprotonated dapdo^{2-} ligand.

It is remarkable that the fragment Ni(2)/Ni(4) in which the two metallic ions are linked by one syn−syn and one monocoordinated carboxylates (together with one oximato bridge from the dapdoH^{-} ligand coordinated to Ni(4)) is identical to the Ni(2)/Ni(1) or Ni(2)/Ni(3) fragments in compound **3**, with bonds parameters very similar too, more details in Tables 4 and 5.

H-Bond Role. Structurally, two aspects make complexes **2** − **4** unanticipated: locally, the variety of ligands attached to each octahedral Ni^{2+} ion and, in a more global sense, the noteworthy, high asymmetry of the final structures. All three compounds present as common traits protonated oxime groups from dapdoH$_2$ and/or dapdoH^{-} ligands, coordinated H$_2$O molecules and noncoordinated O-atoms from monodentate carboxylato groups. Detailed analysis of these fragments reveals their noninnocent role, where the arrangement of such units is led by sets of strong, intramolecular H-bonds that contribute to stabilize the structures. Thus, the necessity of water in the reaction media to obtain the reported complexes can be now understood. Besides, additional crystallization water molecules provide a number of intermolecular H-bonds among the clusters generating extended networks in the crystals. Intramolecular H-bonds for compounds **2**−**4** are summarized in Table S1 in the Supporting Information (including one relevant crystallization water molecule for **3** and the carboxylate anion in **4**). A view of these H bonds within the core of these compounds is shown in Figure 5.

In compound **2** (Figure 5, top), H atoms from the protonated dapdoH$_2$ ligand, the central OH^{-} group and the coordinated molecule of water form a set of H-bonds with O-atoms from the monocoordinated benzoate ligands. This way, benzoate O(9) atom interacts with protonated O(1)-hydroxo and O(3)-oxime atoms, O(10)-benzoate interacts with O(2)-oxime atom, and finally O(12) from the coordinated water molecule interact with O(11)-benzoate atom.

Similarly, in compound **3** (Figure 5, middle), H-atoms from the protonated oximato groups form strong intramolecular H-bonds with the noncoordinated O-atoms of the η^1,μ-AcO ligands (O(2)···O(6) and O(10)···O(12) interactions). In addition, crystallization water molecules are placed between the O-carboxylato atoms coordinated to Ni(2) and coordinated water molecules providing further H-bonds, O(13)···O1w···O(7) and O(14)···O2w···O(4).

In the case of compound **4**, H-atoms from the protonated oximato groups and coordinated water molecules form a set of intramolecular H-bonds that involve the O-atoms from coordinated and anionic carboxylates. Here, the protonated oximato groups form H-bonds with the noncoordinated O-atoms of the η^1,μ-AcO ligands (O(55)···O(62) and O(53)···O(60), respectively). Also, one of the coordinated water molecules interacts in a similar way with the O-atom from the carboxylato coordinated to Ni(3), O(59)···O(68). The three coordinated water molecules form strong H-bonds with the anionic acetate molecule, O(63)···O(58), O(63)···O(68), and O(64)···O(69), folding the molecule. One of the crystallization water molecules joins one deprotonated oximato groups and one monodentate carboxylato

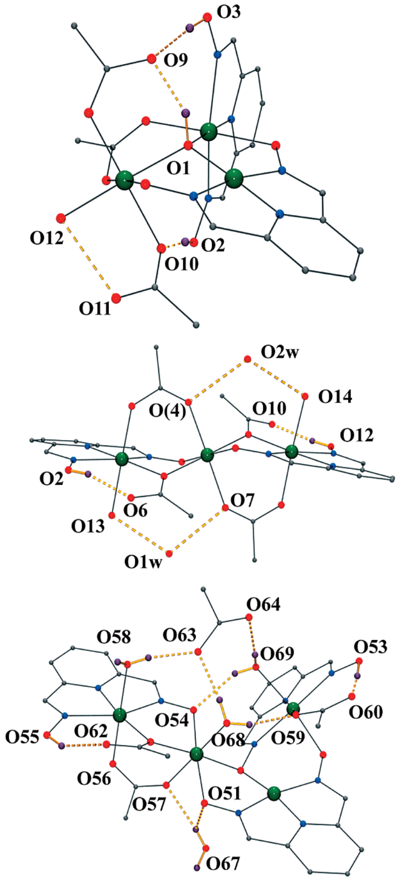

Figure 5. From top to bottom, partially labeled plots of the intramolecular H-bonds for compounds **2**−**4**, in that order. H-atoms not involved in H-bonds, Me groups, aromatic benzoate rings, and parentheses of the labels has been omitted for clarity.

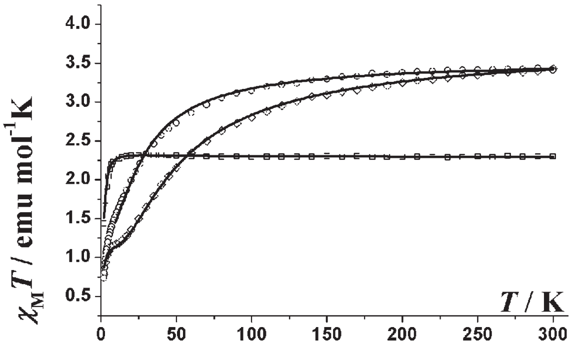

Figure 6. Plot of the $\chi_M T$ product vs T for compounds **2** (squares), **3** (diamonds), and **4** (dot centered circles).

ligand as well, giving as a result weaker interactions, O(67)···O(51) and O(67)···O(57).

Magnetic Measurements and Fit Procedure. Diamagnetic response at room temperature was found for compound **1**, in agreement with the expected results for a cluster containing Ni^{2+} centers with square planar environments. $\chi_M T$ product vs T for compounds **2**−**4** are plotted in Figure 6. Compound **2** shows a $\chi_M T$ value nearly constant between 300 and 14 K with a maximum value of 2.32 cm^3 K mol^{-1} at 30 K. At low temperature, $\chi_M T$ value decreases down to 1.43 cm^3 K mol^{-1}. These room-temperature values are also consistent with the structural data that indicate that one of the nickel atoms, in square planar environment, is diamagnetic. Compound **2** behaves magnetically as a dinuclear system and therefore the fitting of the experimental data was performed by means of the conventional equation derived from the Hamiltonian

$$H = -J(S_1 S_3)$$

for two local $S = 1$ spin centers including an intermolecular interaction parameter zJ'. The subindexes of the local S_n spins along this section refer to the numbers of the corresponding structures. Best fit parameters were $J = +2.16(7)$ cm^{-1}, $zJ' = -0.87(1)$ K, and $g = 2.141(2)$. In good agreement with the above results, magnetization experiments show a magnetization plot that reaches a nonsaturated value 3.3 electrons under an external field of 5 T with an increase versus field lower than the expected for the Brillouin plot for two isolated $S = 1$ centers.

Compound **3** exhibits a room temperature value of 3.43 cm^3 K mol^{-1} which decreases down to 0.82 at 2 K. The $\chi_M T$ plot shows a plateau around 1.15 cm^3 K mol^{-1} and between 5 and 13 K. Analysis of the magnetic data of compound **3** was performed by means of analytical expression derived from the Hamiltonian

$$H = -J(S_1 S_2 + S_2 S_3)$$

which corresponds to a symmetric linear arrangement of three paramagnetic centers where the interaction between the terminal spin carriers have been neglected. Best fit parameters were $J = -18.8(2)$ cm^{-1}, $zJ' = -0.90(3)$ cm^{-1}, and $g = 2.233(3)$. Magnetization plot shows a Brillouin shape behavior supporting the idea of having two electrons as can be expected for a well isolated $S = 1$ ground state.

Tetranuclear compound **4** contains one square planar nickel atom and therefore can be analyzed as a trinuclear system. Room temperature $\chi_M T$ value is 3.41 cm^3 K mol^{-1}, which decreases gradually upon cooling, reaching 0.73 cm^3 K mol^{-1} at 2 K. As it occurred in the previous compound, a change in the slope of $\chi_M T$ plot at values slightly greater than the expected for an $S = 1$ ground state was observed.

In this case, structural data reveals different kind of bridges between the paramagnetic centers of compound **4** and then the experimental $\chi_M T$ plot was analyzed by means CLUMAG program[35] on the two-J Hamiltonian

$$H = -J_1(S_2 S_4) - J_2(S_2 S_3)$$

Best-fit parameters were $J_1 = -16.7$ cm^{-1}, $J_2 = 1.16$ cm^{-1}, and $g = 2.17$. As described above, the Ni(2)/Ni(4) fragment of compound **4** is structurally similar to the one found in **3.** Therefore, J_1 could be related to the exchange parameter of 18.8 cm^{-1} found for **3** and be assigned to the Ni(2)−Ni(4) interaction, whereas the weak interaction J_2 could be related to the single, high torsioned, oximato bridge between Ni(2) and Ni(3). Likewise for compound **3**, here magnetization at 5 T tends to a nonsaturated value associated to two electrons.

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(35) Gatteschi, D.; Pardi, L. *Gazz. Chim. Ital.* **1993**, *123*, 231.

Conclusions

In the present work, we have reported the results obtained using ligand dapdoH_2 together with different nickel salts as precursors. Earlier work with pyridyl monooximato ligands, suggested the possibility of having the neutral ligand, dapdoH_2, or its deprotonated anionic forms, dapdoH^- and dapdo^{2-}, coordinated to Ni centers. The latest, dapdo^{2-}, contains two deprotonated oximato groups conferring the ligand with the capability of increasing the nuclearity and therefore complexity of the final compounds (fact previously observed with manganese). Compounds **1**−**4** are the first examples that corroborate that this is also possible with Ni. From all the above, one of the most relevant results in this preliminary work is the finding of a novel coordination mode for dapdoH^-, 3.20111, which coordinates three Ni^{2+} units, arrangement that was unknown in the chemistry of this dioxime ligand. In addition, another important aspect is the tendency of dapdo^{2-} to force square planar coordination around Ni^{2+} ions, a trait that appears in three of the four compounds described in this paper: **1**, **2**, and **4**. We would also like to stress the capacity of dapdoH_2/dapdoH^-/dapdo^{2-} to coordinate with Ni, providing high nuclearity clusters and new topologies as well as the possibility of achieving octahedral and square planar coordinations around the metallic ions with the use of this ligand. This concept directly affects the magnetic results because square planar coordination around the Ni decreases the total magnetic spin diminishing the superexchange pathways inside the clusters. From a magnetic point of view, this is indeed a limitation in the search of Ni clusters with high spin numbers. Therefore, synthetic strategies should avoid fully deprotonation of the ligand to prevent under aerobic conditions, easy oxidation to Ni^{IV} or square planar coordination.

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Supporting Information Available: H-bond parameters (PDF); crystallographic data files for complexes **1**−**4** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.