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Giannis S. Papaefstathiou<sup>a</sup>; Spyros P. Perlepes<sup>a</sup>

<sup>a</sup> Laboratory of Inorganic Chemistry, Department of Chemistry, University of Patras, Patras, Greece

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## ***Families of Polynuclear Manganese, Cobalt, Nickel and Copper Complexes Stabilized by Various Forms of Di-2-pyridyl Ketone***

**Giannis S. Papaefstathiou and Spyros P. Perlepes**

Laboratory of Inorganic Chemistry, Department of  
Chemistry, University of Patras, Patras, Greece

*The synthetic and structural chemistry of polynuclear manganese, cobalt, nickel and copper carboxylate complexes, stabilized by various forms of di-2-pyridyl ketone, is discussed. The structural diversity displayed by the described complexes stems from the ability of the doubly and singly deprotonated forms of the gem-diol form of di-2-pyridyl ketone, or the monoanion of the hemiacetal form of this ligand, to adopt a variety of coordination modes. The nuclearities of the clusters vary from four to fourteen. Perhaps the most aesthetically pleasing families are the “flywheel”  $\text{Cu}_{12}$  clusters, and the  $\text{Co}_9$  and  $\text{Ni}_9$  complexes in which the nine metal ions adopt a topology of two square pyramids sharing a common apex. A means of increasing the ground-state total spin value of a polynuclear 3d-metal cluster is also proposed. The approach is based on the replacement of hydroxo bridges, that most often propagate antiferromagnetic exchange interactions in clusters, by the end-on azido ligand, which is a well known ferromagnetic coupler. This approach involves “true” reactivity chemistry on pre-isolated clusters and the products are not undergone significant structural changes, except for the azido-for-hydroxo substitution, compared to the starting materials/clusters.*

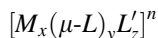
**Keywords:** di-2-pyridyl ketone-based ligands, high-spin molecules, molecular magnetism, polynuclear 3d-metal complexes, X-ray structures

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Address correspondence to Spyros P. Perlepes, Laboratory of Inorganic Chemistry, Department of Chemistry, University of Patras, Patras, Greece.

## A BROAD INTRODUCTION IN THE FIELD OF POLYNUCLEAR 3d-METAL COMPLEXES

Only in the last 15 years have polynuclear complexes of transition metals in moderate oxidation states begun to attract the attention given to high nuclearity compounds of metals in high or low oxidation states.<sup>[1]</sup> The simplest general formula of these assemblies is



where  $M$  is a transition metal ion,  $\mu-L$  a bridging ligand,  $L'$  a terminal ligand,  $x$  is an integer number larger than 3 (and most often smaller than 20), and  $n$  can be zero, a negative, or a positive integer number. This class of compounds is found in the literature with several names such as oligomeric complexes, polynuclear complexes, polymetallic compounds, cages, and clusters. In the current language of inorganic chemistry a “cluster” may take on many meanings; in this article the word “cluster” is used equally to the term “polynuclear complex” for molecules or ions with no metal-metal bonding.<sup>[2]</sup>

A central question here is “Are there methodologies for the rational synthesis of polynuclear complexes?” In general, according to our opinion, the answer is “No.” In contrast to the predictive synthetic schemes of organic chemistry, the reactions in polynuclear transition metal chemistry cannot be described as “under operator control” but instead within the realm of “spontaneous self-assembly.”<sup>[3]</sup> Over the last 10 years, several groups (Christou, Decurtins, Escuer and Vicente, Gatteschi, Hendrickson, Julve, Thompson, Verdager, Winpenny, etc.) have been developing excellent routes to such compounds. Thus, we can loosely speak for strategies. The most important strategies are:

- the “complexes as ligands” strategy;<sup>[4]</sup>
- the more advanced “complexes as metals and complexes as ligands” strategy;<sup>[4]</sup> and
- the “aggregation of relatively small building-block complexes” strategy.<sup>[1,3,5,6]</sup>

Despite the recent development of the above strategies, the most traditional way of preparing such complexes remains the simultaneous employment of suitable bridging and terminal ligands, although with this approach the formation of polymeric species cannot be excluded.

Fascination with polynuclear complexes of metals in moderate oxidation states has existed for at least 150 years.<sup>[7]</sup> Today, polynuclear 3d-metal chemistry is an area of modern science whose interfaces with many disciplines have provided invaluable opportunities for crossing boundaries both within and between the fields of chemistry, physics and biology.

The most exciting new properties of clusters discovered to date have been in the field of magnetism. Molecular clusters of magnetic 3d-metal ions have been of great interest since the discovery that they can function as nanomagnets and show magnetic bistability of pure molecular origin.<sup>[8–10]</sup> The first cluster that was shown to have a very slow (ca. 2 months) relaxation of the magnetization at 2K is the mixed-valent Mn<sup>III/IV</sup> complex<sup>[11]</sup> [Mn<sub>12</sub>O<sub>12</sub>(O<sub>2</sub>CMe)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>]·4H<sub>2</sub>O·2MeCO<sub>2</sub>H **1** with a large spin ground state ( $S = 10$ ),<sup>[12,13]</sup> which has a magnetic hysteresis cycle below 4K similar to that observed for bulk magnets.<sup>[14]</sup> For this reason, clusters that behave like **1** have been called single-molecule magnets (SMMs).<sup>[15]</sup> The magnetic bistability associated with the hysteresis cycle in principle can be used for information storage. The important feature of this compound is that the slow magnetization relaxation is due to the individual molecule rather than to large-range ordering as observed in nanoscale magnetic domains of bulk magnets, as confirmed by several experiments.<sup>[8,16]</sup>

Another unique characteristic **1** at low temperature is that quantum effects dominate the reversal of the magnetization, giving a peculiar step-like magnetic hysteresis cycle.<sup>[17,18]</sup> The system is thus multistable and particularly appealing for potential technological applications, i.e., development of new classes of computers in which quantum coherence is used to store and elaborate information (quantum computers).

The ability of discrete molecules to function as extremely small magnets was a breakthrough in the chemistry and physics of metal clusters because:<sup>8</sup> (1) they are synthesized by solution methods and their samples consist of species with single, sharply defined size; (2) by changing the peripheral ligands, the complex can be made to be more or less soluble, giving advantages in potential applications, e.g., thin film formation; and (3) metal clusters are, in fact, of subnanoscale dimensions—the molecule of **1** has an approximate volume of 2 nm<sup>3</sup>. The first two points represent major advantages of SMMs over nanoscale magnetic particles, and the last point gives hope for the access to the ultimate high-density memory device.

Since the initial discovery, a few classes of the SMMs have been reported. Their formulae and  $S$  values are:

- [Mn<sub>12</sub><sup>III/IV</sup>O<sub>12</sub>(O<sub>2</sub>CR)<sub>16</sub>(H<sub>2</sub>O)<sub>x</sub>](R = Et,  $x = 3$ ; R = Ph,  $x = 4$ )<sup>19</sup> with  $S = 9$  or  $10$ ;
- [Mn<sub>12</sub><sup>III/IV</sup>O<sub>12</sub>(O<sub>2</sub>CR)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>−</sup> with  $S = 19/2$ <sup>20</sup>;
- [Fe<sub>8</sub><sup>III</sup>O<sub>2</sub>(OH)<sub>12</sub>(tacn)<sub>6</sub>]<sup>8+</sup>(tacn = triazacyclononane)<sup>9</sup> with  $S = 10$ ;
- [Fe<sub>4</sub><sup>III</sup>(OMe)<sub>6</sub>(dpm)<sub>6</sub>](dpm<sup>−</sup> = the anion of dipivaloylmethane)<sup>21</sup> with  $S = 5$ ;
- [Fe<sub>10</sub><sup>III</sup>NaO<sub>6</sub>(OH)<sub>4</sub>(O<sub>2</sub>CPh)<sub>10</sub>(chp)<sub>6</sub>(H<sub>2</sub>O)<sub>2</sub>(Me<sub>2</sub>CO)<sub>2</sub>](chp<sup>−</sup> = the anion of 6-chloro-2-pyridone)<sup>22</sup> with  $S = 11$ ;
- [Mn<sub>4</sub><sup>III/IV</sup>O<sub>3</sub>Cl(O<sub>2</sub>CMe)<sub>3</sub>(dbm)<sub>3</sub>](dbm<sup>−</sup> = the anion of dibenzoylmethane)<sup>23</sup> with  $S = 9/2$ ;

- $[\text{Mn}_4^{\text{II/III}}(\text{O}_2\text{CMe})_2(\text{pdmH})_6](\text{ClO}_4)_2$  ( $\text{pdmH}^-$  = the monoanion of pyridine-2,6-dimethanol)<sup>[24]</sup> with  $S=8$  (nonsolvated form) and 9 (solvated form with 2.5 mol of  $\text{H}_2\text{O}$  per mol of complex);
- $[\text{V}_4^{\text{III}}\text{O}_2(\text{O}_2\text{CEt})_7(\text{bpy})_2]$  and  $(\text{Et}_4\text{N})[\text{V}_4^{\text{III}}\text{O}_2(\text{O}_2\text{CEt})_7(\text{pic})_2]$  ( $\text{bpy}$  = 2,2'-bipyridine,  $\text{pic}^-$  = the ion of picolinic acid)<sup>[25]</sup> with  $S=3$ ;
- $[\text{Mn}_{12}^{\text{II/III}}\text{O}_8\text{Cl}_4(\text{O}_2\text{CPh})_8(\text{hpm})_6]$  [ $\text{hmp}^-$  = the anion of 2-(hydroxymethyl)pyridine]<sup>[26]</sup> with  $S=7$ .

After much research, it is now recognized that the unusual properties associated with SMMs require<sup>[8]</sup> a combination of a relatively large spin ( $S$ ) ground state and of a considerable negative magnetic anisotropy. The origin of the negative anisotropy is zero-field splitting in the ground state of a SMM, which arises from single-ion, zero-field splitting at the individual metal ions in the molecule.<sup>[21,24]</sup>

It should be noted that all SMMs discovered to date lose this property above  $\sim 4\text{K}$ , but the important point is that the phenomenon has been established. The present and future generations of researchers will try to raise the critical (blocking) temperature to technologically more useful values, for example above  $77\text{K}$ .

The mission of a synthetic inorganic chemist in the SMMs field is extremely difficult. First, it is difficult enough to design and synthesize molecular clusters with high spin ground states. An unusually large value of  $S$  in the ground state is a result of at least some ferromagnetic exchange interactions between the constituent paramagnetic metal ions within the molecule and/or the presence of spin frustration effects arising in certain topological arrangements of metal ions having competing pair-wise exchange interactions of comparable magnitude.<sup>[27]</sup> The large  $S$  value can be achieved even employing a small number of ions if the individual components have a large spin.<sup>[21]</sup> It must be emphasized at this point that only the ground state of a SMM can be thermally populated at or below the blocking temperatures.<sup>[8]</sup> Today chemists are able to create molecules with large  $S$  values, e.g.,<sup>[28]</sup>  $S=51/2$ , but it will be challenging to have only the ground state populated at  $77\text{K}$ . Second, it is almost impossible to predict the sign and magnitude of the anisotropy of the high spin ground states and much more unpredictable to relate the zero-field splitting of the cluster to those of the single metal ions that are interacting.<sup>[16]</sup>

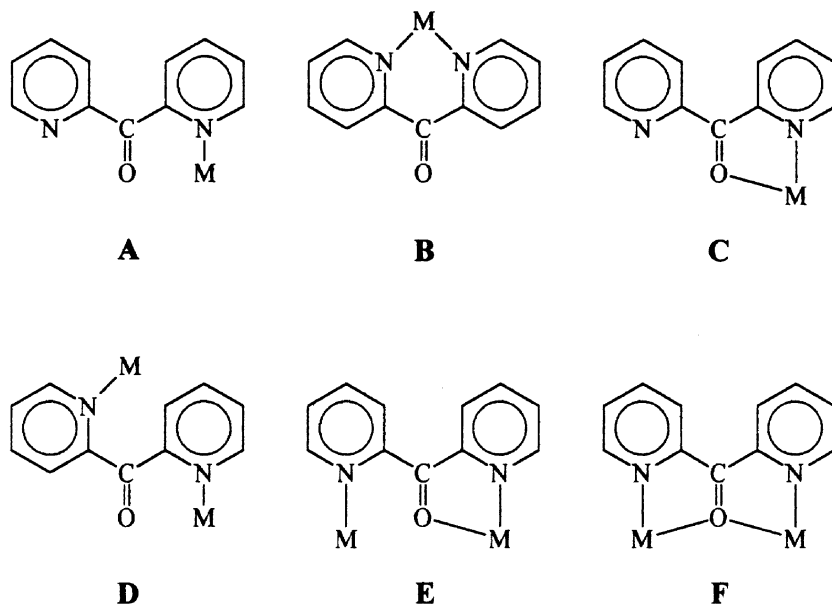
To begin to address the above problems, the synthetic chemist should provide many more polynuclear complexes. The magnetic and spectroscopic study of these species may give exchange couplings and zero-field splittings directly. Thus, a combination of coordination chemistry, structural chemistry, and magnetochemistry may provide new sources of nanomagnetic materials based on molecular clusters and expand our knowledge about the phenomenon of single-molecule magnetism. In many senses this approach is a "try and see" exercise<sup>[1]</sup> as, a priori, there is no means of predicting the structural and magnetic outcome, mainly due to the flexibility of the ligand

systems that lead to polynuclear complexes. This may appear to be strategic weakness, but can be excused in a new field.

We have developed five general reaction systems that almost exclusively, provide polynuclear middle- and late-3d metal complexes performing simple reactions. The subject of this article is the description of the most successful system, which is based on di-2-pyridyl ketone.

## THE LIGATING POTENTIALITIES OF DI-2-PYRIDYL KETONE AND ITS NEUTRAL GEMINAL DIOL AND HEMIACETAL FORMS

Neutral di-2-pyridyl ketone, hereafter abbreviated as  $(py)_2CO$ , has three potential donor groups, the two 2-pyridyl nitrogens and the carbonyl oxygen. It has been found in metal complexes (Figure 1) as terminal, either monodentate (**A**)<sup>[29]</sup> or chelating (**B**, **C**),<sup>[30]</sup> and bridging ( $\mu_2$ )<sup>[29,31]</sup> ligand (**D**, **E**, **F**). The resulting products are mononuclear, dinuclear, trinuclear, or polymeric, depending on the metal ion, the coordination mode of  $(py)_2CO$  (terminal or bridging), and the nature of the anion present.

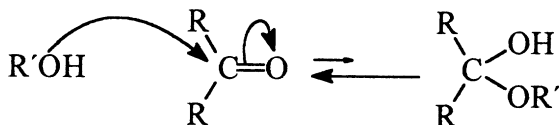


**FIGURE 1** The crystallographically established coordination modes of di-2-pyridyl ketone,  $(py)_2CO$  ( $py$  = 2-pyridyl group).

However, there is a chemical characteristic of  $(\text{py})_2\text{CO}$  that makes this ligand special; this is its carbonyl group. Ketones ( $\text{R}_2\text{CO}$ ) can undergo hydration, with the first step of the reaction involving nucleophilic attack of water on the carbonyl group.<sup>[32]</sup> The tetrahedral intermediate is trapped by reaction with a proton to yield the hydrated form of the ketone, the geminal diol (Figure 2). Similar reactions occur with alcohols as nucleophiles to yield, initially, hemiacetals.<sup>[32]</sup> There is an equilibrium between hydrated forms (or hemiacetals) and ketones in aqueous (or alcoholic) media, which usually lies far over toward the ketone form. If one (or both) of the R groups is strongly electron-withdrawing, e.g.,  $\text{CF}_3$ , the polarization of the C–C  $\sigma$  bond (connecting the R group to the carbonyl) is sufficient to increase the electrophilic nature of the carbonyl carbon and the equilibrium percentage of the hydrated (or hemiacetal) form. The electrophilic character of a carbonyl carbon atom may also be increased by coordination of the carbonyl oxygen to a metal ion (direct polarization) or by coordination of another more remote site in the R groups (induced polarization).<sup>[32]</sup>

The reactions of  $(\text{py})_2\text{CO}$  with metal ions have been particularly well studied over the years. Water and alcohols have been shown to add to the carbonyl group upon coordination of the 2-pyridyl rings to the metal producing the ligands  $(\text{py})_2\text{C}(\text{OH})_2$  or  $(\text{py})_2\text{C}(\text{OR})(\text{OH})$ . This is a relatively long-range effect because there is often no strong interaction of the carbonyl oxygen with the metal center. The neutral ligands  $(\text{py})_2\text{C}(\text{OH})_2$  and  $(\text{py})_2\text{C}(\text{OR})(\text{OH})$  coordinate to the metal centers as tridentate chelates via the two nitrogen atoms and one oxygen atom, with the M–O bond often being weak; the coordination of the alkylated oxygen atom, instead of the hydroxy one, is remarkable. Thus, both neutral ligands do not present interest from the cluster formation point of view leading to mononuclear,<sup>[33]</sup> dinuclear,<sup>[34–36]</sup> or polymeric<sup>[35]</sup> complexes; in the last two cases the metal ions are bridged by anionic ligands present in the complexes, e.g.,  $\text{Cl}^-$  or  $\text{SCN}^-$ .

Completely different and much more interesting (for cluster chemistry) coordination modes are expected—and actually seen—when ligands  $(\text{py})_2\text{C}(\text{OR})(\text{OH})$  and  $(\text{py})_2\text{C}(\text{OH})_2$  are deprotonated. On deprotonation, the former becomes monoanionic, while the latter can function as a monoanion or dianion. The presence of deprotonated hydroxy groups within  $(\text{py})_2\text{C}(\text{OR})\text{O}^-$ ,  $(\text{py})_2\text{C}(\text{OH})\text{O}^-$ , and  $(\text{py})_2\text{CO}_2^{2-}$  is expected to lead to a



**FIGURE 2** The formation of a hydrate ( $\text{R}' = \text{H}$ ) or a hemiacetal ( $\text{R}' = \text{Me, Et, Ph, } \dots$ ) in the reaction of a ketone with water or an alcohol.

great coordinative flexibility, due to the well known ability of the negatively charged oxygen to bridge two or three metal ions. It is not known<sup>[32]</sup> whether the coordination of the oxygen to the metal center occurs after the hydration reaction (in which case we are seeing a polarization effect of the metal upon the hydroxy group leading to its deprotonation) or prior to the reaction, in which case we are seeing a direct activation of the carbonyl toward nucleophilic attack.

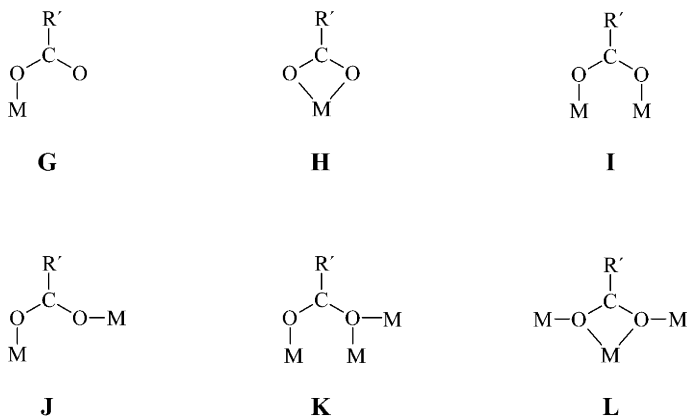
## OUR APPROACH

Our approach for the isolation of molecular clusters has been to target heteroleptic  $R'CO_2^-/(py)_2CO_2^{2-}$ ,  $R'CO_2^-/(py)_2C(OH)O^-$ , and  $R'CO_2^-/(py)_2C(OR)O^-$  complexes of Mn, Co, Ni, and Cu, where  $R' = Me$ ,  $= Me$ , Ph. The reactions between metal carboxylates and  $(py)_2CO$  in  $H_2O$  or  $H_2O$ -containing organic solvents were expected to be a rich source of a variety of polynuclear complexes. Obviously  $(py)_2C(OH)_2$  can be fully or partially deprotonated by the basic carboxylate groups ( $R'CO_2^-$ ); we reasoned that new types of polynuclear  $M/R'CO_2^-/(py)_2C(OH)O^-$  or  $(py)_2CO_2^{2-}$  species might result, as long as the  $R'CO_2^- : (py)_2CO$  ratio was high enough to leave an amount of nonprotonated  $R'CO_2^-$  ions in the reaction mixture, given the fact that both  $R'CO_2^-$  and  $(py)_2C(OH)O^-/(py)_2CO_2^{2-}$  ligands can potentially adopt a great variety of terminal and bridging modes. This has, indeed, turned out to be the case. We also anticipated interesting  $M/R'CO_2^-/(py)_2C(OR)O^-$  species from the reactions between metal carboxylates and  $(py)_2CO$  in alcohols.

Carboxylates are employed for two reasons: First, they are able to deprotonate the hydroxy group(s) of  $(py)_2C(OR)(OH)$  and  $(py)_2C(OH)_2$  under mild conditions (sometimes use of hydroxides perplexes the reactions). Second, they are flexible ligands, a consequence of their capability to adopt a number of different ligation modes, both terminal and bridging, and both monodentate and bidentate.<sup>[37]</sup> The bonding modes exhibited by simple carboxylate ligands in the polynuclear complexes discussed below are shown in Figure 3.

The complexes discussed in the next two chapters are mainly based on our work; however, where a resemblance exists to compounds reported by other groups, such molecules (or ions) have also been included in the discussion. The complexes will be classified according to the coordination modes of the di-2-pyridyl ketone-based ligands. Emphasis is given on the preparative, structural, and reactivity chemistry. It should be noted that reactivity chemistry of polynuclear complexes of 3d-metals in moderate oxidation states is still in its infancy; this is a general method for the preparation of new clusters and a means to modify their physical properties. Brief mention is also made of the magnetic properties of representative clusters.





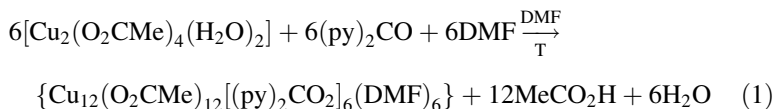
**FIGURE 3** The crystallographically established coordination modes of the simple carboxylate ligands ( $R'CO_2^-$ ;  $R' = \text{Me, Ph}$ ) in the clusters discussed in the next two sections.

Much of the chemistry described below involves the heteroleptic  $R'CO_2^- / (py)_2CO_2^{2-}$ ,  $R'CO_2^- / (py)_2C(OH)O^-$ , and  $R'CO_2^- / (py)_2C(OR)O^-$  ligand sets, plus ligands ( $H_2O$ ,  $ROH$ ,  $OH^-$ ,  $OR^-$ , etc.) derived from the solvents. Each ligand has a specific role to play in stabilizing the structure as the cluster crystallizes.

A final point to be noted is that the chemical and structural identity of the polynuclear complexes is affected by a number of synthetic parameters including the nature of the solvent and the metal ion, the exact  $R'CO_2^- : (py)_2CO$  reaction ratio, and the absence/presence of counter ions, e.g.,  $ClO_4^-$ ,  $PF_6^-$ , in the reaction mixtures.

### POLYNUCLEAR COMPLEXES CONTAINING THE DOUBLY DEPROTONATED GEM-DIOL FORM OF DI-2-PYRIDYL KETONE, $(py)_2CO_2^{2-}$ , AS LIGAND

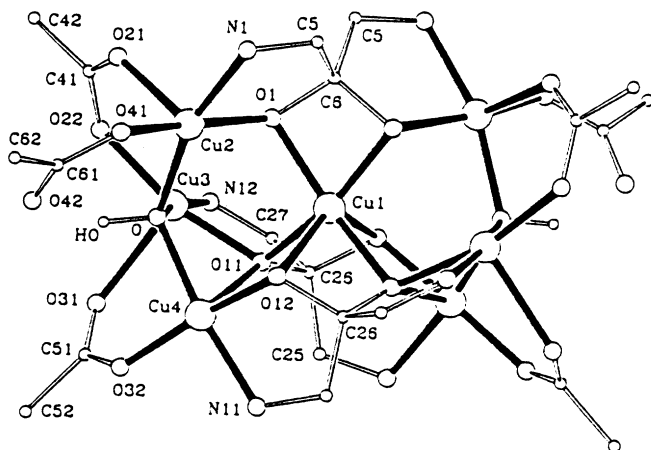
Reaction of  $[Cu_2(O_2CMe)_4(H_2O)_2]$  with one equivalent of  $(py)_2CO$  in hot MeCN gives a mixture of green  $\{Cu_7(OH)_2(O_2CMe)_6[(py)_2CO_2]_3\}$  **2** and violet-blue  $[Cu_{12}(O_2CMe)_{12}\{(py)_2CO_2\}_6]$  **3**. Until recently only the preparation of pure **2** was possible.<sup>[38]</sup> A few months ago we managed to prepare a DMF version of the dodecanuclear cluster, namely complex  $\{Cu_{12}(O_2CMe)_{12}[(py)_2CO_2]_6(DMF)_6\}$  **4**, Eq. (1), without contamination by the heptanuclear cluster.



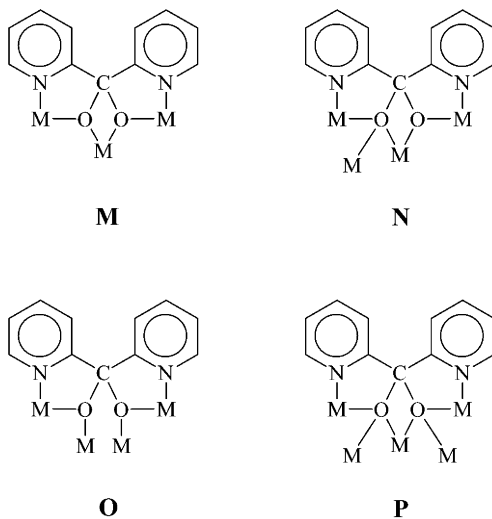
## 4

Complex **2** (Figure 4) has one  $\eta^1:\eta^2:\eta^2:\eta^1:\mu_3 - (\text{py})_2\text{CO}_2^{2-}$  ion (**M**, Figure 5), two  $\eta^1:\eta^2:\eta^3:\eta^1:\mu_4 - (\text{py})_2\text{CO}_2^{2-}$  ions (**N**, Figure 5), four *syn*, *syn*  $\eta^1:\eta^1:\mu_2 - \text{MeCO}_2^-$  groups (**I**), two monodentate  $\text{MeCO}_2^-$  ions (**G**) and two  $\mu_3 - \text{OH}^-$  ions as ligands.<sup>[38]</sup> The seven metal ions form two tetrahedra sharing a common apex at Cu(1). Magnetization measurements at 3K in the field range 0–5 T indicate that the ground state of **2** is  $S = 1/2$ .

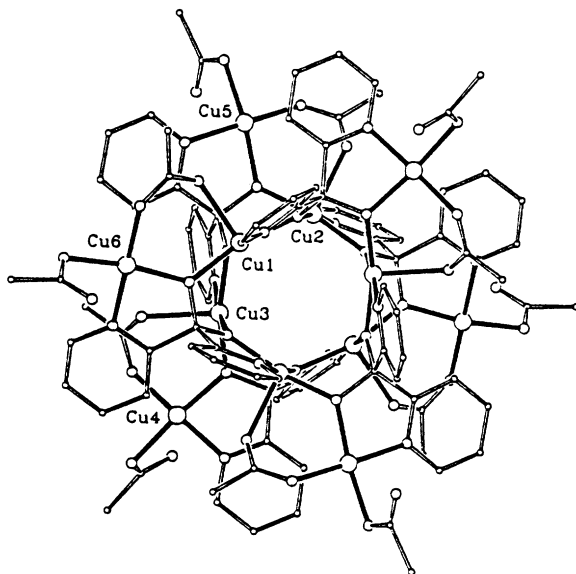
The molecule of **3** (Figure 6) is located on a crystallographic center of symmetry. Inspired by its remarkable structure<sup>[38]</sup> and considering the closest  $\text{Cu} \cdots \text{Cu}$  distances, we refer to this compound as a molecular “flywheel” (Figure 7). From a different point of view, the inner six  $\text{Cu}^{\text{II}}$  centers form a chair-shaped cluster that lies within a cluster consisting of the outer metal ions, Cu(4), Cu(5), Cu(6) and their centrosymmetric equivalents, which also has a chair conformation (Figure 7). All  $(\text{py})_2\text{CO}_2^{2-}$  ligands adopt the  $\eta^1:\eta^2:\eta^2:\eta^1:\mu_4$  coordination mode (**O**, Figure 5), and bridge one outer  $\text{Cu}^{\text{II}}$  center with three  $\text{Cu}^{\text{II}}$  centers of the inner chair. Complex **4** has a very similar structure with **3**; the only difference is that the coordination number of each outer  $\text{Cu}^{\text{II}}$  atom is five in the former because of the coordination of one DMF molecule.



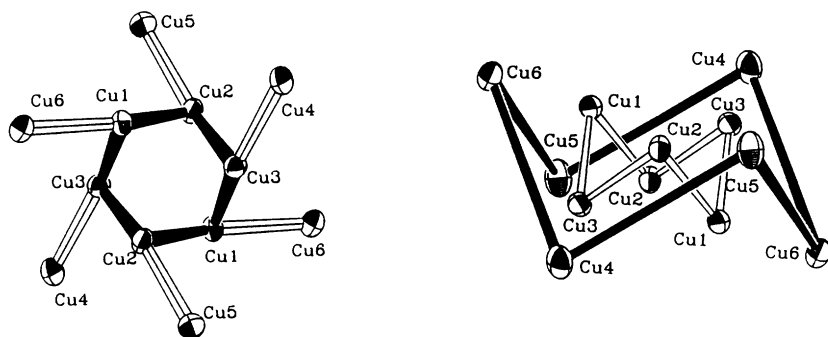
**FIGURE 4** The molecular structure of  $\{\text{Cu}_7(\text{OH})_2(\text{O}_2\text{CMe})_6[(\text{py})_2\text{CO}_2]_3\}$  **2**. Most carbon atoms of the 2-pyridyl rings are omitted for clarity.



**FIGURE 5** The coordination modes shown by the  $(py)_2CO_2^{2-}$  ligand.



**FIGURE 6** The molecular structure of  $\{Cu_{12}(O_2CMe)_{12}[(py)_2CO_2]_6\} \cdot 3$ .



**FIGURE 7** The “fly-wheel” (left) and “chair-within-a-chair” (right) descriptions of the metal topology in the  $\text{Cu}_{12}$  cluster **3**.

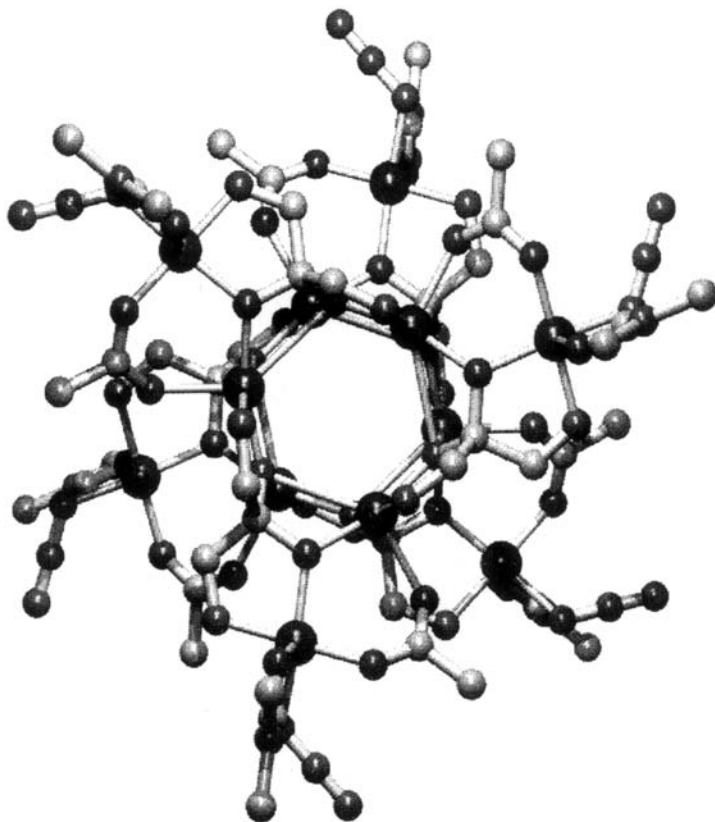
The dodecanuclear complexes **3** and **4** are readily amenable to variation in peripheral monodentate ligation. For example, reaction of **4** with six equivalents of  $\text{NaN}_3$  in hot DMF yields complex  $\{\text{Cu}_{12}(\text{O}_2\text{CMe})_6(\text{N}_3)_6[(\text{py})_2\text{CO}_2]_6(\text{DMF})_6\}$  **5** (Figure 8). The structures of **4** and **5** have a striking similarity; obviously, the replacement of monodentate acetates by azides has no structural effect.

The coordination mode **O** is also shown by the  $(\text{py})_2\text{CO}_2^{2-}$  ligands in the recently reported<sup>[39]</sup> antiferromagnetic octanuclear copper(II) complex  $\{\text{Cu}_8(\text{O}_2\text{CMe})_4[(\text{py})_2\text{CO}_2]_4(\text{pyOH})_4\}(\text{ClO}_4)_4$ , where  $\text{pyOH}$  is 2-hydroxypyridine.

The cobalt(II) carboxylate chemistry of  $(\text{py})_2\text{CO}_2^{2-}$  is exciting.<sup>[40]</sup> Reaction of  $\text{Co}(\text{O}_2\text{CMe})_2 \cdot 4\text{H}_2\text{O}$  with  $(\text{py})_2\text{CO}$  in a 2:1 ratio in MeCN under reflux leads to the nonanuclear complex  $\{\text{Co}_9(\text{OH})_2(\text{O}_2\text{CMe})_8[(\text{py})_2\text{CO}_2]_4\}$  **6**. The double deprotonation of the *gem*-diol form of di-2-pyridyl ketone is a consequence of the high  $\text{MeCO}_2^-$  to  $(\text{py})_2\text{C}(\text{OH})_2$  ratio (4:1) used in the reaction. Complex **6** (Figure 9) is held together by two  $\mu_4\text{-OH}^-$  ions, eight *syn, syn*  $\eta^1:\eta^1:\mu_2\text{-MeCO}_2^-$  groups (**I**) and four  $(\text{py})_2\text{CO}_2^{2-}$  ligands, which adopt the coordination mode  $\eta^1:\eta^3:\eta^3:\eta^1:\mu_5$  (**P**). The central cobalt site,  $\text{Co}(1)$ , is the shared apex of two square pyramids (Figure 10). Each metal... metal edge of the bases is bridged by one acetate, one hydroxo oxygen atom, and one oxygen atom of a  $(\text{py})_2\text{CO}_2^{2-}$  ligand.

The most salient feature of the structure is the coordination number of eight around  $\text{Co}(1)$ , which is extremely rare for cobalt(II). Another unexpected feature of **6** is the two  $\mu_4\text{-OH}^-$  ligands at the center of each base of the double square pyramid.

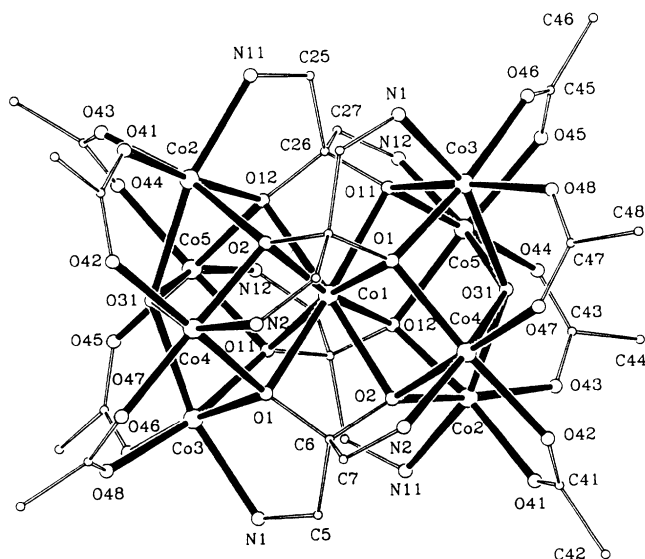
In many polynuclear clusters, like **6**, magnetic exchange interactions are mainly propagated by bridging  $\text{OH}^-$  (or  $\text{O}^{2-}$ ),  $\text{RO}^-$ , or  $\text{R}'\text{CO}_2^-$  ligands, or a combination of two or more of these groups; often these interactions lead



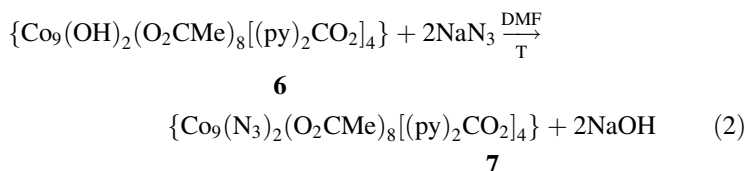
**FIGURE 8** The molecular structure  $\{\text{Cu}_{12}(\text{O}_2\text{CMe})_6(\text{N}_3)_6[(\text{py})_2\text{CO}_2]_6(\text{DMF})_6\}$  **5**.

to antiferromagnetic coupling. An alternative strategy to increase the  $S$  value of the ground state would be the replacement of one or more of the above-mentioned ligands by other groups that are more prone to ferromagnetic coupling. One such ferromagnetic coupler is the azido ligand when it bridges metal ions through one single terminal nitrogen (end-on mode). We have successfully applied this strategy in the case of **6**. While maintaining the thermodynamically stable  $\text{Co}_9$  cage skeleton of **6**, we have been able to modulate the superexchange pathway by substitution of the  $\mu_4$ -hydroxo by unprecedented  $\mu_{1,1,1,1}$ -azido ligands (**Q**). (see Figure 11).

Complex  $\{\text{Co}_9(\text{N}_3)_2(\text{O}_2\text{CMe})_8[(\text{py})_2\text{CO}_2]_4\}$  **7** can be prepared<sup>[41]</sup> either by introducing  $\text{N}_3^-$  ions into the reaction mixture that leads to **6** or by the reaction of pre-isolated **6** with  $\text{N}_3^-$  ions, Eq. (2).

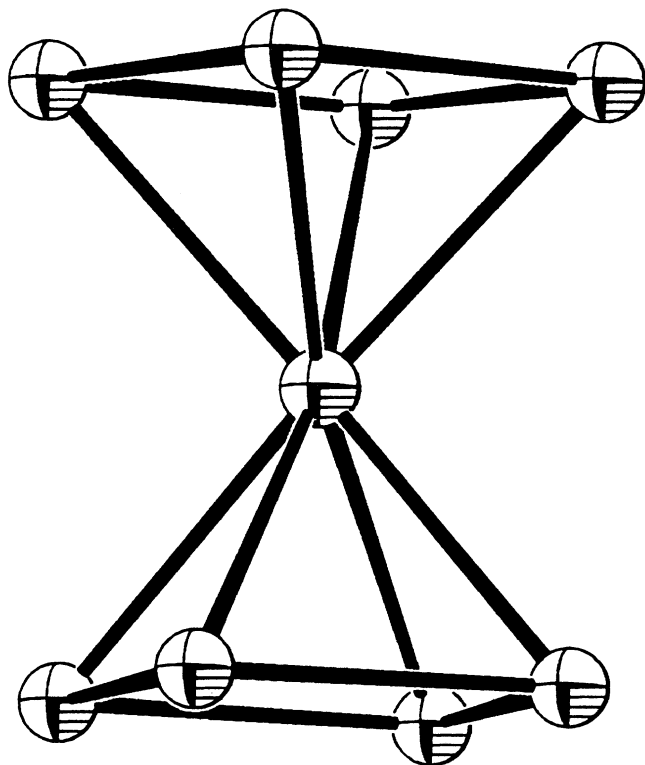


**FIGURE 9** The molecular structure of  $\{\text{Co}_9(\text{OH})_2(\text{O}_2\text{CMe})_8[(\text{py})_2\text{CO}_2]_4\}$  **6**. Most carbon atoms of the 2-pyridyl rings are omitted for clarity.

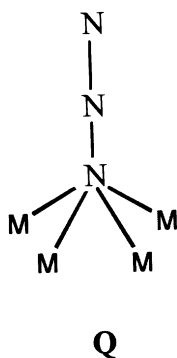


The molecule of **7** (Figure 12) bears striking similarity to that of **6**, showing little structural consequence of the  $\text{N}_3^-$ -for- $\text{OH}^-$  substitution. Complex **7** is the first example of  $\mu_4$  end-on coordination of the azido ligand in inorganic chemistry.

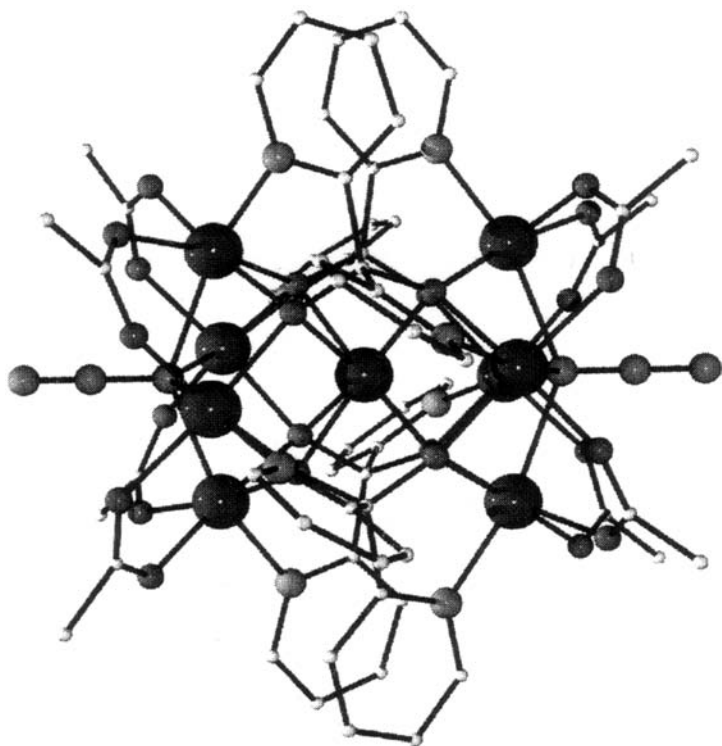
The weak minimum of  $\chi_{\text{M}}T$  at 116K for **7** (Figure 13) is the ferrimagnetic signature of the antiferromagnetic coupling between the central  $\text{Co}^{\text{II}}$  atom and the two ferromagnetically coupled squares in the bases of the cluster. The data for **7** should be associated<sup>[41]</sup> to ferromagnetic coupling mediated by the  $\mu_4$  end-on azido bridges ( $\mu_{1,1,1,1}\text{-N}_3^-$ ) giving a total  $S$  value of seven times the local spin (assuming AF coupling between the central  $\text{Co}^{\text{II}}$  atom and the metal ions of the bases) and leading to the high-spin ferrimagnetic system shown in Figure 14. Thus, the end-on azido ligand is a good substitute for  $\text{OH}^-$  bridges in clusters in order to increase the total spin value ( $S$ ) of the ground state.



**FIGURE 10** The vertex-sharing, double square pyramidal arrangement of the  $\text{Co}^{\text{II}}$  atoms in the  $\text{Co}_9$  cluster **6**.



**FIGURE 11** The novel  $\mu_{1,1,1,1}$  coordination mode of the azido ligands observed in complexes **7** and **11**.

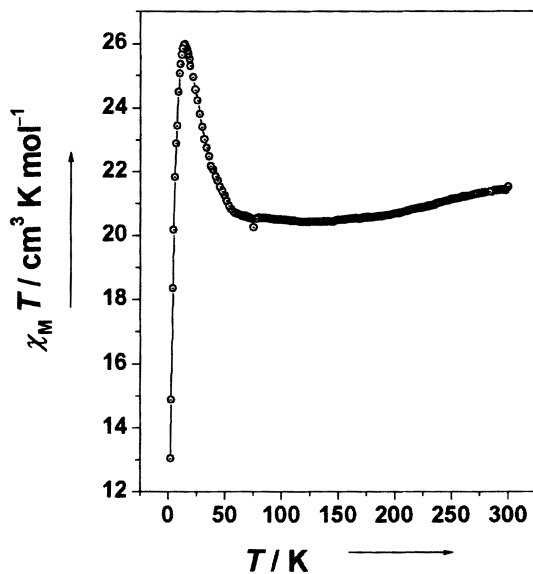


**FIGURE 12** A view of cage  $\{\text{Co}_9(\text{N}_3)_2(\text{O}_2\text{CMe})_8[(\text{py})_2\text{CO}_2]_4\}$  **7**; the size of carbon atoms has been reduced for clarity.

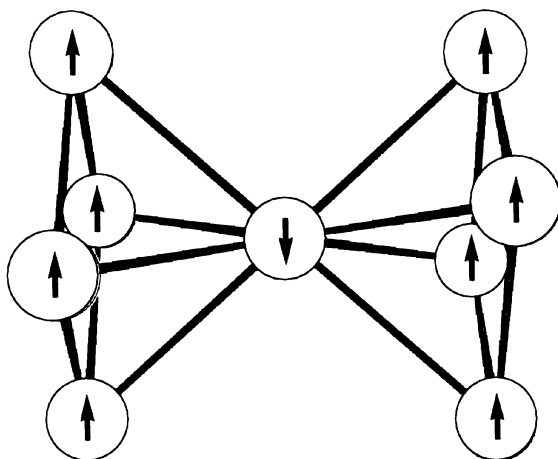
Employment of NaOCN or KCN, instead of  $\text{NaN}_3$ , in procedures analogous to those described by Eq. (2), allows isolation of cages  $\{\text{Co}_9(\text{NCO})_2(\text{O}_2\text{CMe})_8[(\text{py})_2\text{CO}_2]_4\}$  **8** and  $\{\text{Co}_9(\text{NC})_2(\text{O}_2\text{CMe})_8[(\text{py})_2\text{CO}_2]_4\}$  **9**. Their structures are remarkably similar to those of **6** and **7** containing novel  $\mu_4$  end-on (via the N atom) cyanate and cyanide ligands. The  $\text{Co}_9$  skeleton can be considered as a (preformed) host that is able to accommodate small linear anions involving Lewis acid-base interactions. Complexes **8** and **9** exhibit a magnetic behavior similar to that of the parent hydroxo cluster **6**; all three compounds show an overall antiferromagnetic behavior, which may be associated to dominant AF coupling in the  $\text{Co}^{\text{II}}$  square bases of the cage ( $\text{Co}_4$  partial  $S=0$ ) giving a total spin equivalent to one isolated local spin.

The  $\text{Ni}^{\text{II}}/\text{MeCO}_2^-/(\text{py})_2\text{CO}_2^{2-}$  chemistry is completely analogous.<sup>[42]</sup> Complexes  $\{\text{Ni}_9(\text{OH})_2(\text{O}_2\text{CMe})_8[(\text{py})_2\text{CO}_2]_4\}$  **10** and  $\{\text{Ni}_9(\text{N}_3)_2(\text{O}_2\text{CMe})_8[(\text{py})_2\text{CO}_2]_4\}$  **11** have been prepared and structurally characterized; magnetic studies reveal that they have  $S=1$  and  $S=9$  ground states, respectively.





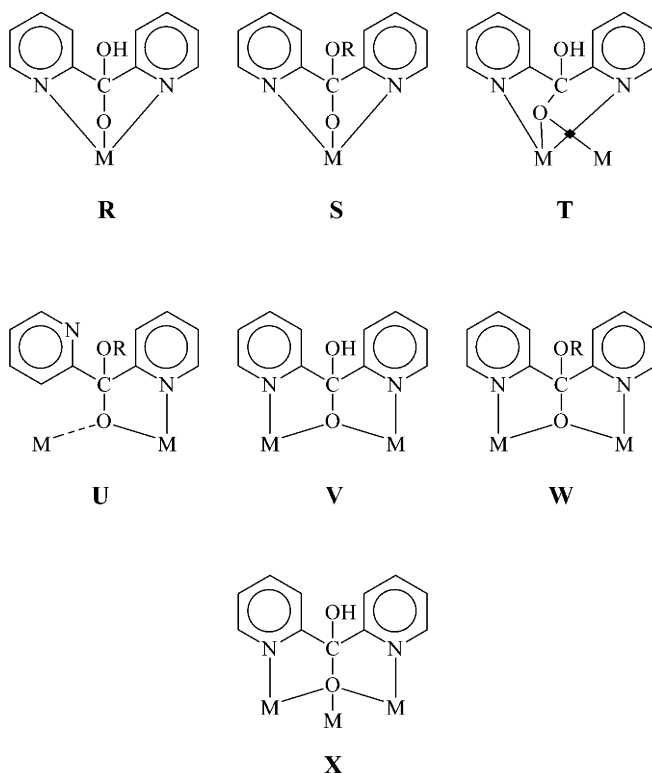
**FIGURE 13** The  $\chi_M T$  versus  $T$  plot for complex  $\{\text{Co}_9(\text{N}_3)_2(\text{O}_2\text{CMe})_8[(\text{py})_2\text{CO}_2]_4\}$  7; the solid line is a guide for the eye.



**FIGURE 14** The high-spin ferrimagnetic description of the  $\text{Co}_9$  azido cluster 7.

# **POLYNUCLEAR COMPLEXES CONTAINING THE MONOANIONS $(py)_2C(OH)O^-$ AND $(py)_2C(OR)O^-$ AS LIGANDS**

The bonding modes exhibited by the monoanionic forms  $(py)_2C(OH)O^-$  and  $(py)_2C(OR)O^-$  are shown in Figure 15. When these ions behave as tridentate chelating ligands (**R**, **S**), the resulting complexes are mononuclear.<sup>43</sup> The  $\mu_2$  coordination (**T**, **U**, **V**, **W**) leads to dinuclear, tetranuclear, or polymeric complexes, mainly depending on the co-ligands present. The  $\eta^1:\eta^3:\eta^1:\mu_3$  coordination mode (**X**) of  $(py)_2C(OH)O^-$  leads to tetranuclear complexes in most cases; the two non-tetranuclear species are found in copper(II) and manganese carboxylate chemistry (vide infra). It is remarkable that the  $\mu_3$  coordination, i.e., analogous to **X**, has not yet



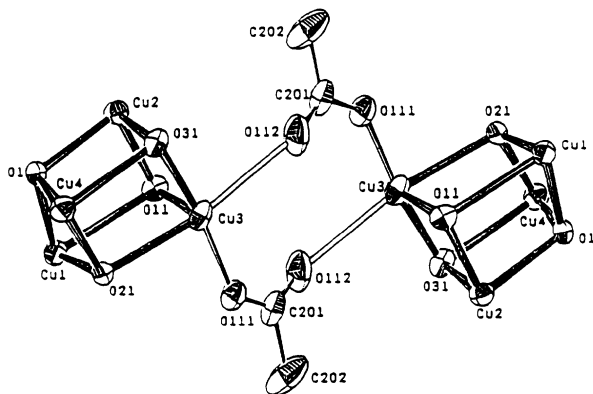
**FIGURE 15** The coordination modes shown by the  $(py)_2C(OH)O^-$  and  $(py)_2C(OR)O^-$  ligands. The dashed line indicates a weak bond.

been found in the metal complexes containing the anions  $(py)_2C(OR)O^-$  as ligands. The mononuclear,<sup>[43]</sup> dinuclear,<sup>[30,44]</sup> and polymeric<sup>[30,36,45]</sup> complexes will not be covered below.

Treatment of  $[Cu_2(O_2CMe)_4(H_2O)_2]$  with 2 equivalents of  $(py)_2CO$  in  $H_2O$  followed by addition of  $NaClO_4$  yields a blue-violet solution that slowly deposits green crystals of  $\{Cu_8(O_2CMe)_4[(py)_2C(OH)O]_8\}(ClO_4)_4$  **12**. The two centrosymmetrically related cubanes in the tetracation of **12** are doubly bridged by two *syn,anti* acetate groups (**J**) connecting two  $Cu^{II}$  atoms (Figure 16).<sup>[46,47]</sup> Each cube is completed by four deprotonated oxygen atoms from the triply bridging  $(py)_2C(OH)O^-$  ligands (**X**, Figure 15) at alternating vertices. Variable-temperature magnetic susceptibility and EPR studies are in line with both an overall antiferromagnetic interaction between  $Cu^{II}$  atoms and the behavior of a simple cubane.<sup>[46]</sup>

The tetranuclear cluster  $\{Cu_4(O_2CMe)_6[(py)_2C(OH)O]_2\}$ , containing the  $Cu^{II}$  atoms in a zigzag arrangement, was obtained<sup>[44]</sup> by Wang's group from the 1:1:1  $[Cu_2(O_2CMe)_4(H_2O)_2]/(py)_2CO/MeCO_2H$  reaction mixture in  $CH_2Cl_2$ . The molecule contains two  $\eta^1:\eta^2:\eta^1:\mu_2-(py)_2C(OH)O^-$  ions (**V**), two monodentate acetates, two *syn, syn*,  $\eta^1:\eta^1:\mu_2-MeCO_2^-$  groups (**I**) and two  $\eta^1:\eta^2:\mu_3-MeCO_2^-$  groups (**K**) as ligands. The intramolecular magnetic interactions between neighboring metal ions are ferromagnetic.

All reported  $R'CO_2^-(py)_2C(OH)O^-$  complexes of  $Co^{II}$  and  $Ni^{II}$  have a cubane structure with the  $(py)_2C(OH)O^-$  ions adopting the coordination mode **X**. These are  $\{Co_4(O_2CMe)_4[(py)_2C(OH)O]_4\}$  **13**,<sup>[40]</sup> its benzoate,<sup>[48]</sup>  $\{Co_4(O_2CPh)_4[(py)_2C(OH)O]_4\}$  **14**; and cationic acetate,<sup>[49]</sup>  $\{Co_4(O_2CMe)_3-[(py)_2C(OH)O]_4(H_2O)\}(ClO_4)$  versions,  $\{Ni_4(O_2CMe)_2[(py)_2C(OH)O]_4(H_2O)_2\}(ClO_4)_2$ <sup>[48]</sup> **15**, and  $\{Ni_4(O_2CMe)_3[(py)_2C(OH)O]_4\}(ClO_4)$ <sup>[49]</sup>.



**FIGURE 16** The “double cubane” structural description of the cation of complex  $\{Cu_8(O_2CMe)_4[(py)_2C(OH)O]_8\}(ClO_4)_4$  **12**.

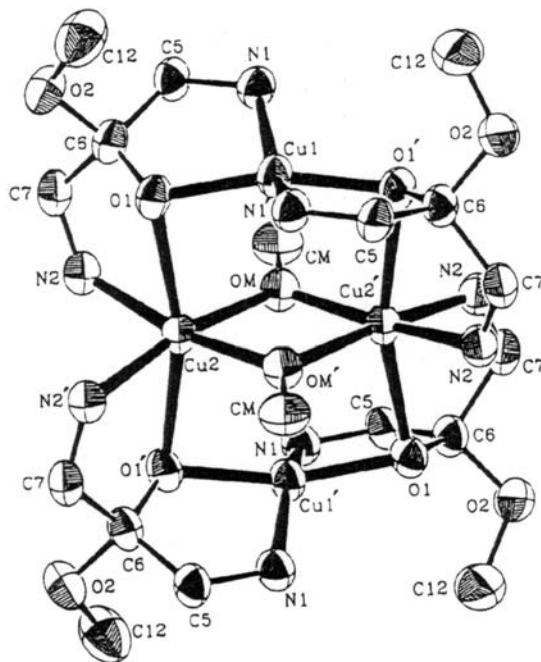
The manganese clusters  $\{\text{Mn}_4(\text{O}_2\text{CMe})_4[(\text{py})_2\text{C}(\text{OH})\text{O}]_4\}^{[50]}$  **16**,  $\{\text{Mn}_4(\text{O}_2\text{CPh})_4[(\text{py})_2\text{C}(\text{OH})\text{O}]_4\}^{[50]}$  **17**, and  $\{\text{Mn}_4(\text{O}_2\text{CMe})_3-[(\text{py})_2\text{C}(\text{OH})\text{O}]_4-(\text{H}_2\text{O})(\text{ClO}_4)^{[50]}$  are isostructural with **13**, **14**, and  $\{\text{Co}_4(\text{O}_2\text{CMe})_3[(\text{py})_2\text{C}(\text{OH})\text{O}]_4(\text{H}_2\text{O})(\text{ClO}_4)$ , respectively. Air oxidation of an MeCN solution of **16** yields the tetradecanuclear mixed-valence cluster  $\{\text{Mn}_{10}^{\text{II}}\text{Mn}_4^{\text{III}}\text{O}_4(\text{O}_2\text{CMe})_{20}[(\text{py})_2\text{C}(\text{OH})\text{O}]_4\}$  **18** containing  $\mu_4\text{-O}^{2-}$  groups, four different types of acetates, and triply bridging (to two  $\text{Mn}^{\text{II}}$  and one  $\text{Mn}^{\text{III}}$  atoms)  $(\text{py})_2\text{C}(\text{OH})\text{O}^-$  ions (**X**, Figure 15) as ligands. The two centrosymmetrically related heptanuclear fragments of **18** are doubly bridged by two acetate groups connecting two  $\text{Mn}^{\text{II}}$  atoms (one from each fragment); these two acetate groups exhibit the rare coordination mode **L** (Figure 3). The magnetic properties of **18** are currently under intense study.<sup>[50]</sup>

There are no reports of polynuclear complexes containing both carboxylate and  $(\text{py})_2\text{C}(\text{OR})\text{O}^-$  ligands. However, the reaction of  $[\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2]$  with two equivalents of  $(\text{py})_2\text{CO}$  in MeOH, in the presence of  $\text{ClO}_4^-$  ions, yields the interesting acetate-free cationic tetranuclear complex  $\{\text{Cu}_4(\text{OMe})_2[(\text{py})_2\text{C}(\text{OMe})\text{O}]_4\}(\text{ClO}_4)_2$  **19**.<sup>[51]</sup>

The four  $\text{Cu}^{\text{II}}$  atoms in the cationic unit of **19** (Figure 17) are coplanar, showing the rare rhombic arrangement. All eight atoms of the  $[\text{Cu}_4(\mu_2\text{-O})_4]^{4+}$  core are coplanar; perpendicular to the plane of the central core is the plane of the  $[\text{Cu}_2(\mu_2\text{-OM})_2]^{2+}$  core, where OM is the oxygen atom of the methoxo group. The  $(\text{py})_2\text{C}(\text{OMe})\text{O}^-$  ions exhibit the coordination mode **W** (Figure 15). The magnetic properties of the compound are characteristic of prevailing antiferromagnetic exchange interactions. The susceptibility data of **19** were fitted with a 3-*J* magnetic model (Figure 18), affording a very strong interaction. ( $J_2 = -490 \text{ cm}^{-1}$ ), a moderate ferromagnetic interaction ( $J_1 = +22 \text{ cm}^{-1}$ ), and a very weak antiferromagnetic interaction ( $J_3 = -0.4 \text{ cm}^{-1}$ ). The energy spectrum of the states, magnetization, and EPR data are in line with an almost degenerate ground state with a magnetic component.

The carboxylates are not crucial for the assembly of the tetranuclear complexes. With the exception of  $\{\text{Cu}_4(\text{O}_2\text{CMe})_6[(\text{py})_2\text{C}(\text{OH})\text{O}]_2\}^{[44]}$  and  $\{\text{Ni}_4(\text{O}_2\text{CMe})_3[(\text{py})_2\text{C}(\text{OH})\text{O}]_4\}(\text{ClO}_4)^{[49]}$  the carboxylates behave as terminal ligands or they do not participate in the clusters (even if the starting materials are metal carboxylates). Several groups have combined the bridging capability of  $(\text{py})_2\text{C}(\text{OH})\text{O}^-$  or/and  $(\text{py})_2\text{C}(\text{OR})\text{O}^-$  with the bridging behavior of other ligands, e.g., chloro ligands and pyrazolates, to prepare tetranuclear clusters with new structural types.<sup>[30,52]</sup>

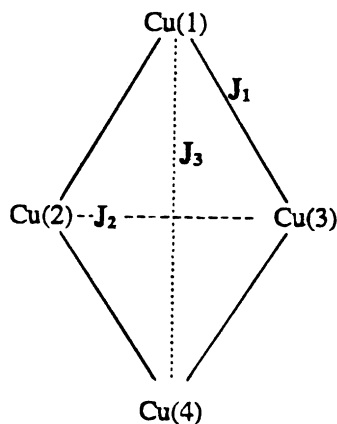
The combination of  $(\text{py})_2\text{C}(\text{OR})\text{O}^-/(\text{py})_2\text{C}(\text{OH})\text{O}^-$  with azido ligands has resulted in structurally and magnetically interesting tetranuclear complexes. Complexes  $\{\text{Mn}_4(\text{N}_3)_4[(\text{py})_2\text{C}(\text{OH})\text{O}]_2[(\text{py})_2\text{C}(\text{OMe})\text{O}]_2\}$  **20** and  $\{\text{Co}_4(\text{N}_3)_4[(\text{py})_2\text{C}(\text{OH})\text{O}]_2[(\text{py})_2\text{C}(\text{OMe})\text{O}]_2\}$  **21** were recently reported by us.<sup>[53]</sup> They can be prepared by the 1:1:1 reaction between  $\text{M}(\text{O}_2\text{CMe})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{NaN}_3$ , and  $(\text{py})_2\text{CO}$  in MeOH ( $\text{M} = \text{Mn}$ ) or MeOH/ $\text{H}_2\text{O}$  ( $\text{M} = \text{Co}$ ) at  $20^\circ\text{C}$ . The structures are very similar (see Figure 19 for the



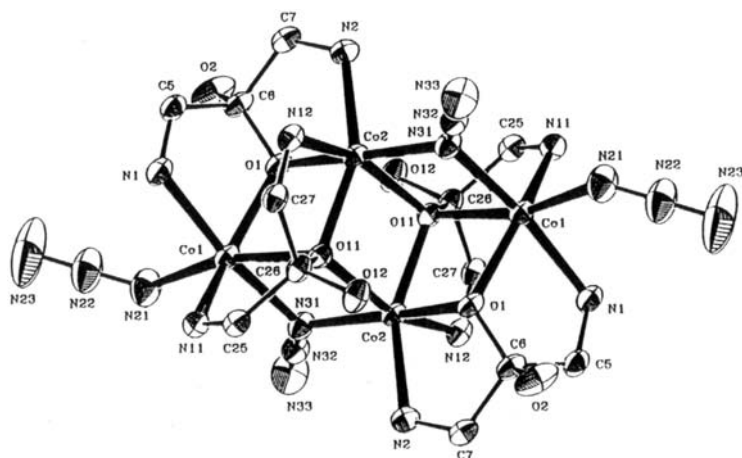
**FIGURE 17** The structure of the cation of complex  $\{\text{Cu}_4(\text{OMe})_2(\text{py})_2\text{-C}(\text{OMe})\text{O}\}_4\}(\text{ClO}_4)_2$  **19**. Most carbon atoms of the 2-pyridyl rings are omitted for clarity.

representative  $\text{Co}^{\text{II}}$  complex). The four metal ions are located at four corners of a defective double cubane (two cubanes sharing one face and each missing one vertex), and bridged by two end-on azido ligands ( $\mu_{1,1}\text{-N}_3^-$ ) and O atoms from the  $(\text{py})_2\text{C}(\text{OH})\text{O}^-$  (**X**) and  $(\text{py})_2\text{C}(\text{OR})\text{O}^-$  (**W**) anions. Peripheral ligation is provided by nitrogen atoms of the two terminal azido ligands and the eight 2-pyridyl rings. Magnetic susceptibility measurements<sup>[53]</sup> in the 2K–300K range indicate a weak antiferromagnetic coupling for **20** and a clear bulk ferromagnetic coupling for **21**; the strong ferromagnetic interaction in the latter is confirmed by the molar magnetization measurement at 2K.

Cortes, Rojo, and coworkers studied the  $\text{Ni}^{\text{II}}/(\text{py})_2\text{CO}/\text{N}_3^-$  chemistry in  $\text{MeOH}/\text{H}_2\text{O}$ . The products are structurally and magnetically, i.e., ferromagnetic, similar to **21**. The only important structural difference between **21** and  $\{\text{Ni}_4(\text{N}_3)_2[(\text{py})_2\text{C}(\text{OH})\text{O}]_2[(\text{py})_2\text{C}(\text{OMe})\text{O}]_2(\text{H}_2\text{O})_2\}(\text{ClO}_4)_2$ <sup>[54]</sup> is that the two terminal azides of the former have been replaced by two terminal  $\text{H}_2\text{O}$  molecules in the latter, thus creating a cationic cluster. The main difference between **21** and  $\{\text{Ni}_4(\text{N}_3)_4[(\text{py})_2\text{C}(\text{OH})\text{O}]_4\}$ <sup>[55]</sup> is that the two  $\eta^1:\eta^2:\eta^1:\mu_2\text{-}$



**FIGURE 18** The exchange pathways in the rhombic cluster **19**. Atoms Cu(3) and Cu(4) of this figure correspond to atoms Cu(2') and Cu(1'), respectively, of the real structure shown in Figure 16.



**FIGURE 19** The molecular structure of  $\{\text{Co}_4(\text{N}_3)_4[(\text{py})_2\text{C}(\text{OH})\text{O}]_2[(\text{py})_2\text{C}(\text{OMe})\text{O}]_2\}$  **21**. Most carbon atoms of the 2-pyridyl rings are omitted for clarity.

$(\text{py})_2\text{C}(\text{OMe})\text{O}^-$  ligands (**W**, Figure 15) of the former have been replaced by two  $\eta^1:\eta^2:\eta^1:\mu_2-(\text{py})_2\text{C}(\text{OH})\text{O}^-$  ligands (**V**) in the latter and, thus, the nickel(II) cluster contains two different types of  $(\text{py})_2\text{C}(\text{OH})\text{O}^-$  ligation (**V**, **X**).

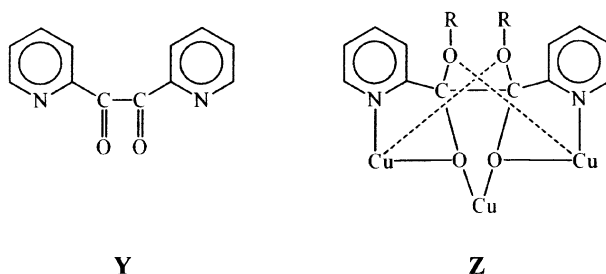
## CONCLUSIONS

Polynuclear complexes (molecular clusters) of 3d-metal ions are an interesting class of compounds that have recently given new opportunities for testing and developing sophisticated theories of mesoscopic matter.<sup>[56]</sup> As such, they are a very good meeting point for chemists and physicists. These materials also have a large technological potential (information storage in one molecule, quantum computers). Whether this is only a dream depends—from the chemistry viewpoint—on the synthetic work of many inorganic chemists who should try to learn how to organize a large number of metal ions in clusters and accept the challenge to collaborate with physicists. The complicated nature of many of the clusters known proves that they would not have been targeted using rational synthetic principles. Therefore, it seems that there is presently no control of structure (and hence properties).

We hope that this article illustrates what is possible in the area of polynuclear transition metal complexes through very simple coordination chemistry. The anions of the *gem*-diol and hemiacetal forms of di-2-pyridyl ketone have fulfilled their promise as a source of polynuclear Mn, Co, Ni, and Cu complexes with interesting structures and properties. The immense structural diversity of the complexes described here stems from the ability of the  $(\text{py})_2\text{CO}_2^{2-}$  and  $(\text{py})_2\text{C}(\text{OH})\text{O}^-/(\text{py})_2\text{C}(\text{OR})\text{O}^-$  ligands to exhibit no less than nine distinct coordination modes (Figures 5 and 15). Presumably, the presence of dissimilar donor atoms within these ligands leads to this great coordinative flexibility, however, their versatility was unexpected. Employment of carboxylates in the  $(\text{py})_2\text{CO}_2^{2-}$  chemistry gives an extraordinary structural flexibility in the mixed  $\text{R}'\text{CO}_2^-/(\text{py})_2\text{CO}_2^{2-}$  systems (“blends”<sup>[57]</sup>) as illustrated in complexes **2–11** and  $\{\text{Cu}_8(\text{O}_2\text{CMe})_4(\text{py})_2\text{CO}_2\}_4(\text{pyOH})_4\}(\text{ClO}_4)_4$ .<sup>[39]</sup>

Several research groups have contributed to the coordination chemistry of  $(\text{py})_2\text{CO}$ -based ligands. Our main contribution is two fold: First, the realization that  $(\text{py})_2\text{C}(\text{OH})_2$  can be doubly deprotonated leading to structurally impressive clusters and, secondly, the introduction of novel  $\mu_{1,1,1,1}$ -azido ligands into the chemistry of  $(\text{py})_2\text{CO}_2^{2-}$  as a means to increase the *S* value of the ground state of the cobalt(II) and nickel(II) clusters; the latter approach is being developed in collaboration with the group of Escuer and Vicente at Barcelona. Our results also suggest that for structures of this complexity, understanding the relationships between structure and magnetic ground states is still difficult.

We believe that the area of molecular clusters based on the anionic forms of di-2-pyridyl ketone is still at the beginning. The reactions of other 3d-metals (especially vanadium, chromium, and iron) with  $(\text{py})_2\text{CO}$  should be studied in detail, considering how interesting the magnetic properties of the products could be. For example, high-spin iron(III) (*S* = 5/2) is a promising building block to obtain large *S* values in the ground state.



**FIGURE 20** The formula of 2,2'-pyridyl,  $(\text{py})_2\text{COCO}$  (**Y**) and the crystallographically established coordination mode of its  $\text{Cu}^{\text{II}}$ -mediated alcoholysis product  $(\text{py})_2\text{C}(\text{OR})\text{OC}(\text{OR})\text{O}^{2-}$  (**Z**;  $\text{R} = \text{Et}, \text{Pr}^n$ ). The dashed lines indicate weak bonds.

Other unpredictable ligands, which present chemical similarities to  $(\text{py})_2\text{CO}$ , as a means of stabilizing polynuclear coordination assemblies, are also worthy of study. More recently, our efforts have turned toward the use of 2,2'-pyridyl,  $(\text{py})_2\text{COCO}$ , **Y** in Figure 19) that contains an extra donor group compared to  $(\text{py})_2\text{CO}$ , to see how incorporation of this ligand type might affect the structures and physical properties of the products. We have just reported<sup>58</sup> that simple reactions involving a blend of  $(\text{py})_2\text{COCO}$  and carboxylate ligands in alcohols produce a series of structurally and magnetically interesting, planar pentanuclear copper(II) complexes of the general formula  $\{\text{Cu}_5(\text{OH})_2[(\text{py})_2\text{C}(\text{OR})\text{OC}(\text{OR})\text{O}]_2(\text{O}_2\text{CR}')_4(\text{ROH})_2\}$ , where  $\text{R} = \text{Et}, \text{Pr}^n$  and  $\text{R}' = \text{Me}, \text{Ph}$ . The  $\text{Cu}^{\text{II}}$ -mediated alcoholysis of  $(\text{py})_2\text{COCO}$  gives the bis(hemiacetal) dianions  $(\text{py})_2\text{C}(\text{OR})\text{OC}(\text{OR})\text{O}^{2-}$  which behave as  $\eta^1:\eta^2:\eta^1:\eta^2:\eta^1:\mu_3$  ligands (**Z**, Figure 20).

For polynuclear 3d-metal complexes, the chemistry and physics in the last decade of the second millennium have been brilliant. We look forward to seeing what synthetic chemists and physicists can create in this area in the first decade of the third millennium. Our belief is that the future will also be brilliant.

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