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Adventures in the Coordination Chemistry of Di-2-pyridyl Ketone and Related Ligands: From High-Spin Molecules and Single-Molecule Magnets to Coordination Polymers, and from Structural Aesthetics to an Exciting New Reactivity Chemistry of Coordinated Ligands

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Dedicated to Prof. Nick Hadjiliadis on the occasion of his retirement[‡]

Keywords: Cluster compounds / Coordination modes / Coordination polymers / Magnetic properties / N,O ligands

The coordination chemistry of di-2-pyridyl ketone and related ligands is reviewed. An outline of the variety of such ligands is presented. References are given to methods for the synthesis of ligands that are not available on the market. The activation of the carbonyl group(s) of some of the ligands towards further reactions seems to be an emergent area of synthetic inorganic chemistry. The coordination chemistry of each ligand with metals is briefly described. Emphasis is placed on structural features and physical properties (mainly magnetic) of the resulting metal clusters and coordination polymers. The structural diversity of the complexes stems from the ability of the deprotonated diol- or hemiketal-type ligands to adopt a variety of bridging coordination modes depending on the number of carbonyl groups, the nature of the extra donor groups in the molecule and on the reaction conditions. Employment of a second organic or inorganic ligand in this chemistry gives an extraordinary structural flexibility in the resulting mixed-ligand systems. The initial use of 1,1′-carbonyldiimidazole and 1,1′-oxalyldiimidazole in copper(II) chemistry, which leads to unprecedented coordination polymers containing alcoholysis and/or hydrolysis "fragments" of the ligands, is also illustrated.

1. Organization of This Microreview and General Information

This Microreview presents a focused overview of the coordination chemistry of ligands with the general formulae X–CO–X, X–CO–Y, X–CO–CO–X, and X–CO–X–CO–X, where X and Y are donor groups. We mainly describe the polynuclear metal complexes (clusters) and coordination polymers that have derived from the use of these ligands and the organic chemistry of their metal complexes. From the viewpoint of properties, emphasis is placed on the magnetism of the metal complexes. Much of the chemistry, both published and unpublished, that is reported comes from our group; however, detailed reference to all appropriate work by others is provided. The Microreview aims not to be comprehensive in terms of a discussion of every known cluster or coordination polymer containing a ligand derived from the above-mentioned molecules; rather, it aims to provide the reader with some idea of the range of chemistry that has been carried out (and indeed remains still to do) with these ligands. The article contains eight sections, including this one. The next section is introductory: the reader can find brief, general information on the two classes of compounds that are frequently mentioned in this Microreview, namely metal clusters and polymers, as well as a short discussion of the organic chemistry of metal complexes, which is currently a popular topic in inorganic chemistry. The last part of Section 2 provides a "hors d'oeuvre" of the ligands that are discussed in detail in Sections 3–7. Section 8 provides initial conclusions and perspectives for future research. Sections 2 and 3 are divided into parts for clarity. The organization of this Microreview in sections and parts is presented below.

[‡] In recognition of his great contribution to the advancement of Inorganic Chemistry in Greece.

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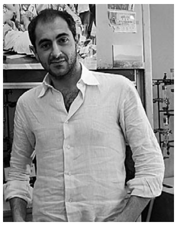
Review articles on the coordination chemistry of the ligands X–CO–Y, X–CO–CO–X, and X–CO–X–CO–X have never appeared. The majority of the metal complexes of these ligands have been prepared only in the recent years, and much of their chemistry remains to be explored in more detail. Some families of polynuclear Mn, Co, Ni, and Cu complexes stabilized by various forms of di-2-pyridyl ketone, prepared before 2001, were briefly reviewed in 2002.[1] Selected developments (published in the period 2005–2007) in the 3d metal cluster chemistry of ligands based on di-2-pyridyl ketone with magnetic relevance have recently been included in a small section of a broad Perspective covering diol-type ligands.[2]

The method currently used to describe the binding of polydentate ligands to multiple metal centers involves a mixture of Greek letters and sub- and superscripts; this η/μ notation is sometimes confusing. An alternative is the "Harris Notation".[3] The Harris notation describes the binding mode as $X.Y_1Y_2Y_3\cdots Y_n$, where X is the overall number of metal ions bound by the whole ligand, and each value of Y refers to the number of metal ions attached to the different donor atoms. The order of Y groups follows the Cahn–Ingold–Prelog priority rules, hence (for most of the ligands included in this report) O comes before N. In the case of complicated chelating/bridging ligands, to distinguish between several alternatives, a subscripted number is included to show to which metal center the donor is attached. In the following, the binding modes of the ligands are often described by using the Harris notation. Since the reader always has recourse to diagrams, we avoid using subscripted numbers in most cases. Occasionally we use the currently approved notation based on the Greek letters μ



Theocharis C. Stamatatos completed his BSc and PhD degrees at the University of Patras (Greece), the latter under the supervision of Professor Spyros P. Perlepes. He then joined Professor George Christou's group, where he worked for 2.5 years as a postdoctoral researcher. His research interests are focused on the synthesis and magnetochemical characterization of oligo- and polynuclear 3d and 3d/4f metal complexes. He has been awarded the Young Investigator Award for 2007 by the Executive Committee of the American Chemical Society (ACS), Division of Inorganic Chemistry (DIC). He has also been selected by the MAGMANet European Network of Excellence for one of the three best Doctoral Theses in Molecular Magnetism in 2008 (ADocMolMag prize). He is co-author of 70 papers, including two reviews, in peer-reviewed journals.

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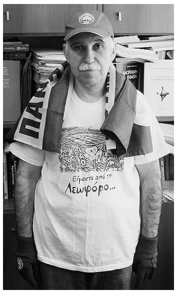


Spyros P. Perlepes was born in Athens (Greece) in 1953. He was appointed Professor of Inorganic Chemistry at the University of Patras in 2001. He had previously been a Lecturer and Assistant Professor at the University of Ioannina (Greece), before moving to Patras (1992) as Associate Professor. His university education (BSc, PhD) was at the University of Patras. He spent post-doctoral and sabbatical periods (for ca. 6 years) with Dr. David Nicholls at the University of Liverpool (UK), Professor Herman O. Desseyn at the University of Antwerp (Belgium), and Professor George Christou at the Universities of Indiana and Florida. Research in his group focuses upon the chemistry of molecular 3d, 4f, and 3d/4f metal clusters and coordination polymers, with emphasis on their magnetic and optical properties. He is co-author of more than 280 scientific papers, including four reviews, in peer-reviewed journals and three General and Inorganic Chemistry books (in Greek). He is currently in the Editorial Board of "Polyhedron" and "Spectrochimica Acta Part A" and serves as Associate Editor in "Bioinorganic Chemistry and Applications". He is a fan of Frank Sinatra, The Beatles, and The Beach Boys. He is a football maniac, being a fanatical supporter of Panathinaikos F. C.

and η. It is our belief that the Harris notation is, at least for the ligands discussed in this Microreview, more convenient than the notation based on Greek letters.

2. A Broad Introduction

The term "ligand" (Latin *ligare*, to bind) was first proposed by Alfred Stock when lecturing in Berlin on borane and silane (1916), but it did not come into extensive use among English-speaking chemists until the 1940s and 1950s, largely through the popularity of Jannik Bjerrum's PhD thesis.[4] The proper use of old ligands and the design of new ones underlies much of modern coordination chemistry. Classical coordination chemistry employed simple, or relatively simple, ligands, e.g. NH_3, en, Cl^-, H_2O. However, the use of a variety of complex, polydentate ligands, e.g. cyclic polydentate ligands, crown ethers, cryptands, sepulchrates, and ligands of unusual reach, which are designed to achieve specific purposes, continues to be an important frontier of research in inorganic chemistry.[5] Theoretical concepts related to such and other specialized ligands are the chelate effect, the macrocyclic effect, the conformation of chelate rings, and the isoelectronic and isolobal relationships. Before dealing in depth with the ligands that are the subject of this Microreview, we give brief information on polynuclear metal complexes and coordination polymers, some of which can be synthesized by the use of these ligands, as well as on "organic" reactions promoted, catalyzed, or initiated by metal ions, since in some of them metal complexes of the title ligands are important starting materials.

2.1. The Field of Polynuclear 3d Metal Complexes (Clusters)

There continues to be a great interest[6] in the synthesis and physicochemical study of polynuclear complexes (clusters[7]) containing paramagnetic metal ions. Among the reasons for this is the search for oxide-bridged metal clusters of various nuclearity to model M_x sites in biomolecules, including the goals of understanding the assembly of the multinuclear Fe^{III}/O^{2-} core of the iron-storage protein ferritin[8] and elucidating the nature and mechanism of action of the $CaMn_4$ core of the H_2O oxidizing complex within the photosynthetic apparatus of green plants and cyanobacteria.[9] In addition, 3d and mixed 3d/4f metal clusters often display interesting and sometimes novel magnetic properties, including high ground-state spin values, currently up to $S = 83/2$,[10] and single-molecule magnetism. Single-molecule magnets (SMMs)[11] are zero-dimensional molecular systems displaying slow relaxation of their magnetization vector as a result of the combination of a large ground-state spin and a significant magnetic anisotropy of the Ising (or easy axis) type, the latter being reflected in a negative zero-field splitting parameter *D*. Thus, such molecules exhibit magnetization hysteresis loops, the classical property of a magnet. The maximum value of the barrier *U* to magnetization relaxation (reorientation, reversal) is given by $S^2|D|$ or $(S^2 - 1/4)|D|$ for integer and half-integer *S* values, respectively. Due to their small size, SMMs straddle the classical/quantum interface in also displaying quantum tunneling of magnetization,[12] quantum phase interference,[13] and exchange biasing,[14] which are properties of the microscale. SMMs have been proposed for several potential applications[15] including high-density information storage, molecular spintronics, and as qubits for quantum computation. Important advances in the technology of SMMs involve preparation of partially ordered Langmuir–Blodgett films of SMMs,[16] their organization on conducting[17] and functionalized Si(100) surfaces,[18] their deposition onto a polycarbonate surface,[19] and development of processes for magnetic information storage on polymers[20] by using patterned SMMs.

The first SMM reported was $[Mn^{III}_8Mn^{IV}_4(H_2O)_4O_{12}(O_2CMe)_{16}]$,[21,22] with $S = 10$ and $D = -0.50\ cm^{-1}$ (–0.72 K). Although Mn clusters containing some Mn^{III} ions have to date proven to be the most fruitful source of SMMs, complexes displaying SMM behavior are known for several other 3d metals (V^{III}, Fe^{II}, Fe^{III}, Co^{II}, Ni^{II}), mononuclear lanthanide species, and combinations of 3d with 4d, 5d, and 4f paramagnetic metal ions.[11] The record values today of the effective energy barrier to magnetization reversal (U_{eff}) and the blocking temperature (T_B, the temperature below which the properties appear) are 86.4 K and approximately 4.5 K, respectively, for cluster $[Mn^{III}_6(EtOH)_6(Et\text{-}sao)_6O_2\{O_2CPh(Me)_2\}_2]$[23] ($S = 12$, $D = -0.43\ cm^{-1}$), where Et-sao^{2-} is the dianion of 2-hydroxyphenylpropanone oxime. A recent, exciting development in the chemistry of SMMs is their rational assembly into 1D, 2D, and 3D coordination networks, giving rise to original magnetic properties.[24]

2.2. Why Coordination Polymers?

The utilization of organic polymers, mainly composed of the elements C, H, O, N, and, to a lesser extent, some neighboring main group elements such as B, Si, P, and S, in the 1960s transformed the way in which we live. The metallic elements, which comprise more than half of the elements in the Periodic Table, had until the early 1990s contributed almost nothing of important value to the field of polymers beyond their occasional use in the catalysis by which polymers are made. However, this situation has changed in the last 15 years or so; the reason is that metal ions have attractive features for new generations of metalloorganic polymers,[25] which are also known as coordination polymers,[26a] metal–organic coordination networks (MOCNs), metal–organic frameworks (MOFs),[26b] or organic–inorganic hybrid materials (in the cases where the metal–organic connectivity is interrupted by "inorganic" bridges or where an extended inorganic metal-containing network possesses only terminal organic ligands). These metal–ligand compounds may extend "infinitely" into one, two, or three dimensions (1D, 2D, or 3D, respectively). At least in one extended dimension the metal ions must solely be bridged by an organic ligand. Further, at least one C atom must lie between the donor atoms. It is the bridging organic ligands which allow for the large diversity in the topologies and possible properties of the metal–organic coordination networks.

The process of building a coordination polymer is principally directed by the coordination bond. Weaker interactions, such as hydrogen bonding, π–π stacking, metal–metal interactions based on d^{10} metal cations (Cu^I, Ag^I, Au^I), and metal–aromatic interactions are important for the packing of the 1D chains, 2D nets, and 3D frameworks.[25] By carefully selecting the ligand (mainly the organic one) and the metal ion, scientists aim to tune the physical properties and thus realize various applications of coordination polymers in catalysis, electrical conductivity, luminescence, magnetism, nonlinear optics, molecular electronics, drug delivery, sensing, and zeolitic behavior.[25,27] The ultimate goal is the transformation of some coordination polymers to functional materials. Coordination polymers are also significant from a structural chemistry perspective: new, intriguing molecular topologies are discovered, and numerous examples of interesting phenomena such as the interpenetration of networks are provided.[28] The structures of some minerals such as diamond,[29] quartz,[30] rutile,[31] perovskite,[32] PtS,[33] zeolite,[34] and feldspar[35] have been artificially produced by "replacing" monatomic anions, e.g. O^{2-} and S^{2-}, with polyatomic organic ligands as linkers and utilizing metal centers (with well-defined coordination geometries) as nodes.

2.3. Approaches for Making Clusters and Coordination Polymers

The chances of identifying novel types of clusters or coordination polymers with improved or new properties will be increased by the development of new reaction systems with suitable organic ligands or combinations of organic and inorganic ligands. The success of organic chemists in establishing methods for making large, complicated molecules and organic polymers in a systematic and controlled manner is one of the great collective achievements of twentieth-century science. The attitude involved in such a process has become inculcated in all synthetic chemists, where they look for molecules to be built step by step. By comparison, transition-metal chemists have made little progress in discovering general approaches to preparing compounds containing large or infinite numbers of metal centers. This is because until recently means for routine characterization of such compounds did not exist, and because the obvious biological relevance and commercial applications of large organic molecules and large organic polymers were not matched by properties of polynuclear and polymeric metal complexes. The lack of control in transition-metal chemistry has led to the neologism "self-assembly".[36]

In the last decade, several groups have been introducing an element of design into the assembly process by choosing rigid ligands that have strong preferences for specific bonding modes and metal ions with preferred coordination geometries. This "designed assembly" approach has produced many beautiful clusters[37] and coordination polymers.[26b,27h,38] The structures of such compounds are moderately predictable on the basis of the preferred coordination geometry of the metal ion, the number of preorganized donor sites presented by the ligand, and the limited flexibility of the ligand. Typical examples of such rigid ligands are the cyanido ion[39] and various tailored derivatives of 4,4′-bipyridine.[25,40]

Other researchers, including our group, use much less well-behaved *bridging* organic ligands for the preparation of clusters[41] and coordination polymers.[42] Once formation of five- or six-membered chelate rings is limited or excluded, the coordinative flexibility of any polydentate ligand increases enormously.[36] This flexibility in turn allows the stabilization of many unpredictable structures, almost invariably incorporating further ligands such as hydroxido, oxido, other inorganic anions, alkoxido ligands, or solvate molecules. In the case of clusters, this approach has been termed "serendipitous assembly".[43] The advantages of serendipitous assembly in cluster chemistry and of less-designed (or "non-programmed") assembly in the chemistry of coordination polymers are considerable. Most often, designed assembly requires similar coordination at each metal site, and this restricts the number of accessible structures, e.g. to Platonic solids, rings, and grids in the case of cluster chemistry.[36] On the other hand, serendipitous or less-designed assembly vastly increases the range of compounds available for study. The unusual structures of some of such compounds can lead to novel properties. It is clear, however, that we cannot simply trust our luck in making such clusters and polymers; there has to be considerable forethought in the ligands, metals, and conditions (reactant ratio, pH, solvent, etc.) for any significant progress to be made.[44] Carboxylato, pyridonato, polyalcoholato, and pyridylalcoholato bridging ligands are frequently used in this chemistry.[2,44,45] The deprotonated oxygen atoms of these ligands are not coordinatively saturated by binding to one metal, and therefore act as bridges, leading to the build-up of larger metal clusters or polymers.

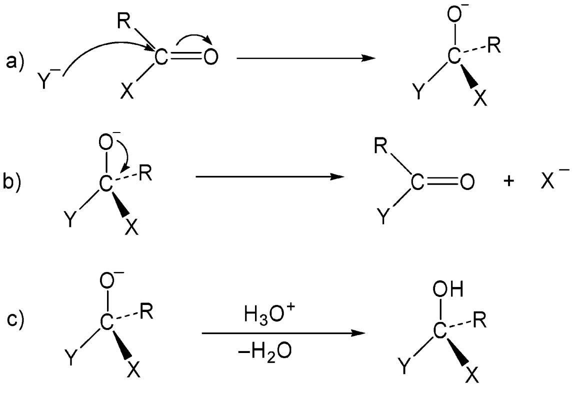
As the fields develop, the boundary between "designed" and "serendipitous" assembly becomes blurred: examples are the many beautiful compounds reported by Saalfrank and co-workers[6b] and the ground-state spin-switching of clusters by targeted structural distortion studied by Brechin and co-workers.[46]

2.4. Reactivity of Coordinated Carbonyl Compounds

While polynuclear and polymeric metal complexes are most often synthesized by the reaction of the metal precursor and a presynthesized ligand, it is also possible to generate the ligands in situ from an easily available organic compound. This approach allows the reactivity of the metal ion to activate a proligand, transforming it through an in situ reaction, sometimes providing coordination compounds with ligands not accessible by conventional organic synthesis.[47]

Whereas the effect of the ligands upon a metal ion is well understood and rather satisfactorily quantified, the converse effect is not so. There are two main reasons for this.[48] Firstly, a metal ion is a discrete center (even in a polynuclear/polymeric system) and, to a certain extent, its orbitals have many of the properties of hydrogen-like atomic orbitals. In contrast, ligands are frequently polynuclear species, in which the orbitals of the donor atoms are also involved in intraligand covalent bonding. Secondly, the ligand donor orbitals may be more or less polarizable than metal orbitals. In particular, the change from lone pair to bonding pair, upon the formation of the coordinate bond, has effects on the other atoms or groups, which might be bonded to the ligand donor atom(s). A metal ion may alter the properties of a coordinated ligand via conformational, polarization, and π-bonding changes.[48] These effects and their combination are the origins of the modification of ligand reactivity that is observed in coordination compounds. This modification is a currently "hot" research theme in modern transition-metal chemistry.

Reactions of coordinated carbonyl groups with *free*[49] nucleophiles are particularly interesting.[48,50] The reason for this is that carbonyl compounds are of great importance in the formation of C–C bonds in organic chemistry, and metal-ion control of their reactivity offers a way to promote, inhibit, or control such reactions. There are two types of reactions of carbonyl compounds. In the first type, the nucleophile reacts with the electrophilic C atom of a carbonyl group to generate a tetrahedral center (Scheme 1a). The fate of this tetrahedral intermediate is dependent upon the nature of the substituents R and X and upon the incoming nucleophile Y^-. If X^- is a better leaving group than Y^-, the overall reaction is a nucleophilic substitution of X by Y (Scheme 1b). If X^- is not a better leaving group than Y^-, then either Y^- is lost (no overall reaction) or a substituted alcohol can be formed by reaction of the tetrahedral organic anion with an oxonium ion (Scheme 1c). In many cases the alcohol may then undergo further reactions.

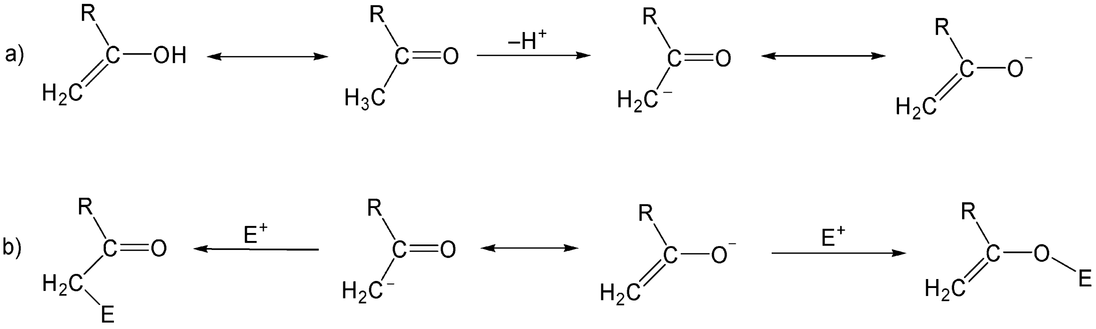


Scheme 1. (a) The reaction of a free nucleophile with a carbonyl compound. (b) Collapse of the tetrahedral intermediate with the formation of a new carbonyl compound. (c) Trapping of the tetrahedral intermediate with an oxonium ion to generate an alcohol.

The second type of reaction pattern with carbonyl compounds involves the generation of a nucleophilic enol or enolate ion. The generation of the latter requires a base (Scheme 2a) and the putative nucleophile may act as a general base. The enol or enolate C atom is nucleophilic and may react with electrophiles. In other cases, the electrophile can react with the O atom (Scheme 2b).

Both of the above-mentioned reactivity types of a carbonyl compound may be modified by coordination to metal ions. As a result of the polarization effect, the electrophilic character of a carbonyl C atom may be increased by coordination of the O atom to the metal center, and thus any reactions in which the rate-determining step is nucleophilic attack upon this site might be accelerated. In a similar manner, the presence of a positively charged metal coordinated to the O atom might favor enolization and accelerate reactions in which enolization or reaction of an enolate is rate-determining.[48] The pK_a of the enol is also sensitive to O coordination, and this may facilitate the formation of the enolate.

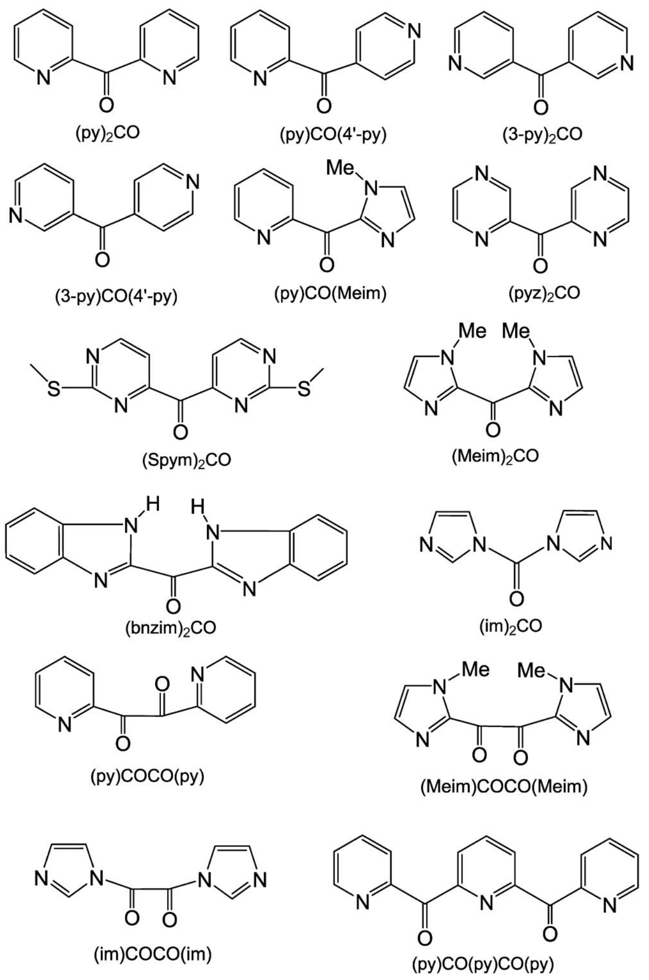
Numerous examples of metal-ion modification of reactions of carbonyl compounds are known, and some will be mentioned later.



Scheme 2. (a) Generation of enol molecules and enolate anions from a carbonyl group. (b) Reactions of an enolate anion with an electrophile (E^+) at carbon or oxygen.

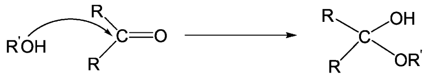
2.5. The Ligands X–CO–X, X–CO–Y, X–CO–CO–X, and X–CO–X–CO–X (X, Y = Donor Groups)

The carbonyl-based ligands, whose metal cluster and polymer chemistry is discussed in this Microreview, are shown in Scheme 3. Only in few cases are the ligands incorporated intact in their metal complexes. In most cases, the ligands are transformed or decomposed upon coordination.



Scheme 3. The carbonyl-based ligands discussed in this Microreview.

We showed in Scheme 1 that the tetrahedral intermediate that is initially formed from the reaction of a nucleophile with a carbonyl compound may further react in a number of different ways. Many of the reactions of the ligands shown in Scheme 3 proceed along the pathway indicated in Scheme 1c. The hydration of ketones is a reaction analogous to the hydrolysis of an ester:[48] the first step of the reaction involves nucleophilic attack of H_2O on the carbonyl group. The tetrahedral intermediate is trapped by reaction with a proton to yield the hydrated form of the ketone, the *geminal* diol, $R_2C(OH)_2$ (Scheme 4). Similar reactions occur with alcohols (R′OH) as nucleophiles to yield, initially, hemiketals $R_2C(OH)(OR')$. In practice, there is often an equilibrium between hydrated forms and ketones in an aqueous solution, although the equilibrium usually lies far over towards the ketone form.[48] If, however, one (or both) of the R groups is electron-withdrawing (such as CF_3, CCl_3, or a 2-pyridyl group), the polarization of the C–C σ bond connecting the R group to the carbonyl C atom is sufficient to increase the electrophilic nature of the carbonyl C atom and the equilibrium percentage of the hydrated form. This suggests that, in metal ion-mediated hydrations of ketones, it might not be necessary for the carbonyl O atom to be coordinated to the metal center: the induced polarization from another more remote coordination site might be sufficient. In the following discussion, there are many examples in which one or two ketone groups in the polydentate ligands of Scheme 3 are attacked by H_2O or an alcohol to give products analogous to those in Scheme 4. The reactions of $(py)_2CO$ (Section 3) are such examples.



Scheme 4. The formation of a hydrate (*gem*-diol, R′ = H) or a hemiketal (R′ = alkyl or aryl) in the reaction of a ketone with H_2O or an alcohol.[48]

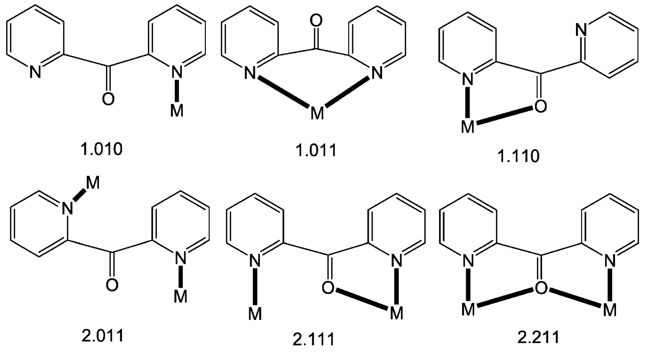
In some cases the free carbonyl ligand exhibits *very high* reactivity toward nucleophilic reagents, which leads to its decomposition, because of the *strong* electron attraction exerted from both sides on the carbonyl group by the heterocycle. Thus, at the outset of our efforts we were aware that such ligands could not be incorporated in metal complexes in, e.g. aqueous or alcoholic reaction media. However, we hoped that such reactions would likely give metal clusters or polymers containing bridging decomposition "fragments" of the original ligands. This, indeed, has turned out to be the case (vide infra).

3. The Rich Coordination Chemistry of Di-2-pyridyl Ketone, $(py)_2CO$

3.1. General Information

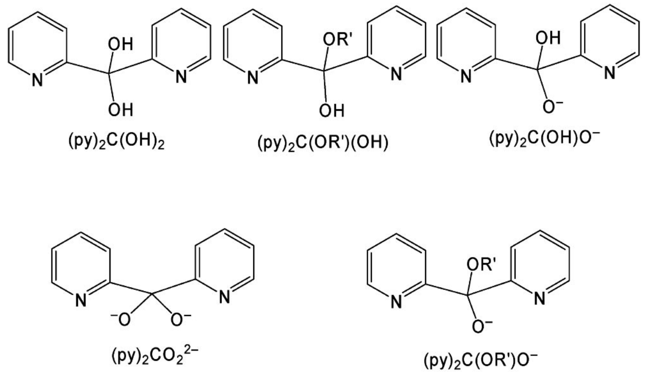
The reactions of $(py)_2CO$ with metal ions (mainly 3d metal ions) have been well studied over the years.[1,2,48]

Neutral $(py)_2CO$ (Scheme 3) has three potential donor groups, the two 2-pyridyl nitrogen atoms and the carbonyl oxygen atom. This group has been found in metal complexes as terminal ligand, either in the 1.010 monodentate or in the chelating (1.011, 1.110) mode, and as a bridging (2.011, 2.111, 2.211) ligand (see Scheme 5). The resulting products are mononuclear,[51] dinuclear,[52] polynuclear or polymeric; examples of the latter two families of complexes are reported in parts 3.2 and 3.3.

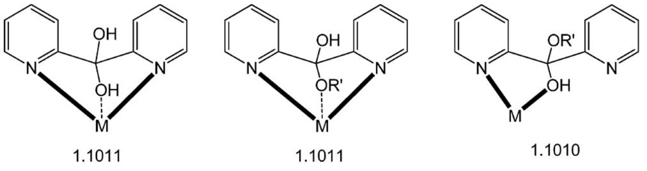


Scheme 5. The crystallographically confirmed coordination modes of $(py)_2CO$ (py = 2-pyridyl) and the Harris notations[3] that describe these modes.

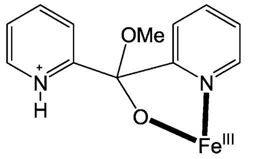
A range of nucleophiles, including H_2O and alcohols (R′OH), have been shown to add to the carbonyl group *upon coordination of the carbonyl oxygen atom and/or the 2-pyridyl rings* forming the ligands $(py)_2C(OH)_2$ [the *gem*-diol of $(py)_2CO$, Scheme 6] and $(py)_2C(OR')(OH)$ [the hemiketal form of $(py)_2CO$], respectively. Sometimes this is a relatively long-range effect[48] – there is often no direct interaction of the carbonyl O atom with the metal center. The neutral ligands coordinate to the metal ions as *O*,*N*,*N′* chelates (1.1011), the M–O bond often being weak (see Scheme 7); the coordination of the alkylated O atom in many complexes, instead of the hydroxyl one, is remarkable. Thus, the two neutral ligands do not hold interest from the viewpoints of cluster or polymer formation,[1,2] leading to mononuclear,[53] dinuclear,[53c,54] or polymeric[54b] complexes; in the latter two cases the metal ions are bridged by anionic ligands. Representative examples are $[Er(NCS)_3\{(py)_2C(OEt)(OH)\}_3]$ (**1**),[53a] $[Co_2Cl_4\{(py)_2C(OMe)(OH)\}_2]$ (**2**)[54a] and $[Cu(NCS)_2\{(py)_2C(OMe)(OH)\}]_n$ (**3**).[54b] Of particular interest is the zwitterion $(^+Hpy)(py)C(OMe)O^-$ that is present in complex $[Fe_4(dbcat)_4\{(Hpy)(py)C(OMe)O\}_2\{(py)_2C(OMe)O\}_2](ClO_4)_2$ (**4**),[55] where $dbcat^{2-}$ is 3,5-di-*tert*-butylcatecholate(–2); this ion is bound in a bidentate 1.101 fashion forming a five-membered chelating ring (Scheme 8). Also remarkable is complex $[Cu\{(py)_2C(OH)_2\}_2](H_2F_3)_2$ (**5**), in which the $H_2F_3^-$ anion exists as a HF_2^-/HF adduct (rather than a F^-/2HF species) as evidenced by IR spectroscopy and X-ray crystallography.[53o]



Scheme 6. Structural formulae of the neutral and anionic ligands that derive from the addition of H_2O or alcohols (R′OH) to the carbonyl group of $(py)_2CO$. Note that none of these ligands exist as free species; they only exist in their respective metal complexes.



Scheme 7. Frequently observed terminal coordination modes for $(py)_2C(OH)_2$ and $(py)_2C(OR')(OH)$. The dashed line indicates a weak bond.



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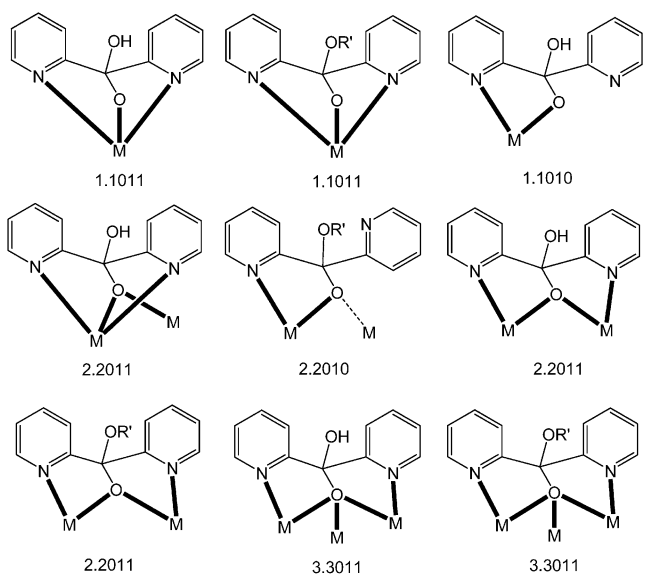
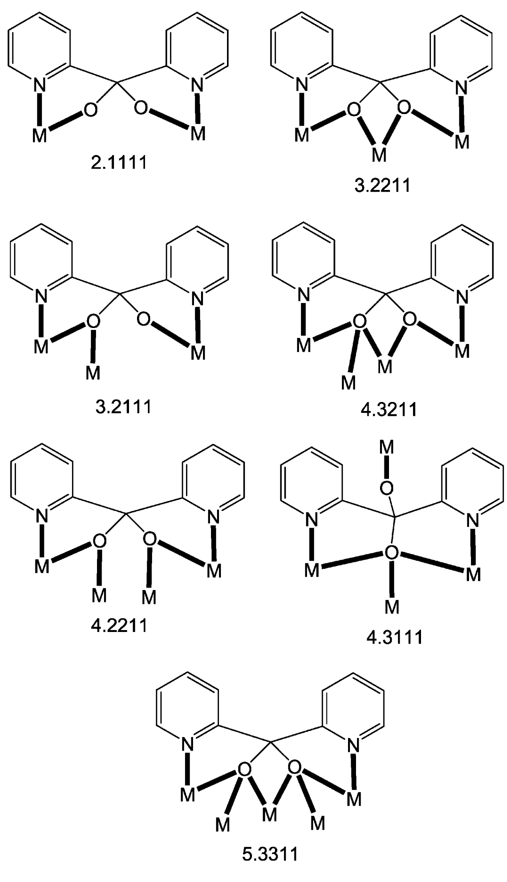
Scheme 8. The 1.101 coordination mode of the unique zwitterionic ligand $(^+Hpy)(py)C(OMe)O^-$ that is present in complex $[Fe_4(dbcat)_4\{(Hpy)(py)C(OMe)O\}_2\{(py)_2C(OMe)O\}_2](ClO_4)_2$ (**4**).

Completely different and much more interesting (for metal cluster and polymer chemistry) coordination modes are seen when the *gem*-diol and the hemiketal ligands are deprotonated. Upon deprotonation, the latter becomes monoanionic, while the former can function either as mono- $[(py)_2C(OH)O^-]$ or dianionic $[(py)_2CO_2^{2-}]$ (see Scheme 6).[1,2] The presence of deprotonated hydroxyl groups (alkoxido groups) leads to a great coordinative flexibility due to the well-known ability of the negatively charged oxygen atom to bridge two or three metal ions. The monoanionic $(py)_2C(OH)O^-$ and $(py)_2C(OR')O^-$ ligands usually bridge two (μ_2) or three (μ_3) metal centers, while $(py)_2CO_2^{2-}$ can bridge as many as five metal sites. It is not known[48] whether the coordination of the O atom to the metal center occurs after the hydration reaction (in which case we see a polarization effect of the metal ion upon the hydroxyl group leading to its deprotonation) or prior to the reaction, in which case we see direct activation of the carbonyl group toward nucleophilic attack. The immense structural diversity displayed by the complexes reported stems in part from the ability of $(py)_2C(OH)O^-$, $(py)_2C(OR')O^-$, and $(py)_2CO_2^{2-}$ to exhibit no less than 16 distinct coordination modes (Schemes 9 and 10).[1,2] Employment of carboxylates (RCO_2^-) and/or inorganic anions (Cl^-, NO_3^-, N_3^-, NCO^-, SO_4^{2-}, etc.) as ancillary ligands in the reaction mixtures gives an extraordinary structural flexibility in the mixed-ligand systems, allowing the synthesis of a variety of metal clusters (with nuclearities ranging from 3 to 26) and coordination polymers with interesting structures and magnetic properties.



Scheme 9. The coordination modes shown by the $(py)_2C(OH)O^-$ and $(py)_2C(OR')O^-$ ligands and the Harris notations[3] that describe these modes. The dashed line indicates a weak bond. Note that both μ_2 $(py)_2C(OH)O^-$ ligands have the same Harris notation, i.e., 2.2011. In order to distinguish between these two alternatives, we may write[3] 2.201_11_1 and 2.201_11_2; the subscripted number shows the metal center to which the donor is attached. The figure is reproduced from ref.[123] by permission.



Scheme 10. The coordination modes shown by the $(py)_2CO_2^{2-}$ ligand.

It is worth mentioning that the bridging ligands form simultaneously chelating rings, which give the products thermodynamic stability.

3.2. The Chemistry and Magnetism of Recently Reported Homometallic Clusters with $(py)_2CO$-Based Ligands

Several groups[56] have contributed to the metal cluster chemistry of $(py)_2CO$-based ligands. The main contribution of our group during the earlier stages, i.e., before 2002, of this research project was twofold:[1,2] First, the realization that $(py)_2C(OH)_2$ can be doubly deprotonated to form $(py)_2CO_2^{2-}$ (Scheme 6) and increase enormously its coordination potential, thus leading to structurally interesting clusters, e.g. to a "flywheel" Cu^{II}_{12} cluster[57] and to Co^{II}_9[58] and Ni^{II}_9[59] clusters with an apex-shared double square-pyramidal metal topology. Second, the introduction of novel 4.400 azido (end-on quadruply bridging) ligands into the $M^{II}_9/OH^-/(py)_2CO_2^{2-}$ chemistry (M = Co, Ni) as a general means to increase the ground-state *S* value of 3d metal clusters leading to high-spin molecules; this approach often involves "true" reactivity chemistry on preisolated clusters.[59,60]

In the following text in this section, we describe developments in the *homo*metallic cluster chemistry and magnetochemistry of $(py)_2CO$, published in the period 2002–2008. The organization of the material is based on the metal used.

The employment of $(py)_2CO$ in *manganese* acetate chemistry, which had been communicated in 2003,[61a] was recently reported[61b] in detail. The reaction of $Mn(O_2CMe)_2\cdot 4H_2O$ with one equivalent of the ligand in Me_2CO gives $[Mn^{II}_4(O_2CMe)_4\{(py)_2C(OH)O\}_4]$ (**6a**) as summarized in Equation (1). The tetranuclear molecule **6a** has a cubane topology in which the Mn^{II} and the deprotonated O atoms from the 3.3011 ligand (Scheme 9) occupy alternate vertices of the cube, as shown in Figure 1. The magnetic properties of this complex have been modeled with two *J* values, which reveal weak antiferromagnetic interactions within the molecule. A similar reaction in $MeCN/H_2O$ in the presence of ClO_4^- ions yields the cationic complex $[Mn_4(O_2CMe)_3\{(py)_2C(OH)O\}_4(H_2O)](ClO_4)$ (**6b**), whose cation also has a cubane structure.[62]

$$4Mn(O_2CMe)_2\cdot 4H_2O + 4(py)_2CO \rightarrow [Mn_4(O_2CMe)_4\{(py)_2C(OH)O\}_4] + 4MeCO_2H + 12H_2O \quad (1)$$

Complex $[Mn^{II}_{10}Mn^{III}_4O_4(O_2CMe)_{20}\{(py)_2C(OH)O\}_4]$ (**7**)[61b] is obtained from the 1:1 reaction, in $EtOH/CH_2Cl_2$, between $Mn(O_2CMe)_2\cdot 4H_2O$ and $(py)_2CO$ in the presence of NEt_3, according to Equation (2). The core of **7** consists of two mixed-valence cubane $\{Mn^{II}_2Mn^{III}_2(\mu_3\text{-}O)_2(\mu_3\text{-}OR'')_2\}^{4+}$ subunits that are linked through an unusual $\{Mn^{II}_6\}$ moiety via eight 2.11 $MeCO_2^-$ groups (see Figure 2). Although we were far from understanding the mechanism of the reaction that leads to **7**, we speculated[61b] that the oxides formed by the hydrolysis processes attack the preformed Mn^{II}_4 cubane **6a**, replacing two $(py)_2C(OH)O^-$ ligands with a concomitant oxidation of two Mn centers, thus expanding the nuclearity of the cluster (through μ_3-

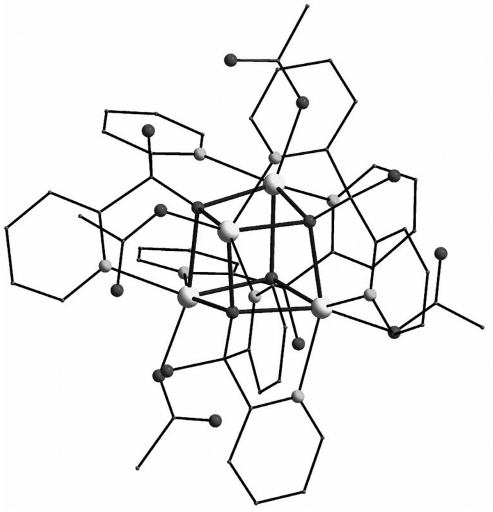


Figure 1. The molecular structure of complex $[Mn_4(O_2CMe)_4\{(py)_2C(OH)O\}_4]$ (**6a**). The cubane core is highlighted.

O^{2-} to μ_4-O^{2-} conversion) by incorporation of six Mn^{II} ions between two $Mn^{II}_2Mn^{III}_2$ cubane subunits. The complex has a low $S = 1 \pm 1$ ground-state value.

$$14Mn(O_2CMe)_2{\cdot}4H_2O + 4(py)_2CO + O_2 + 8NEt_3 \rightarrow [Mn^{II}_{10}Mn^{III}_4O_4(O_2CMe)_{20}\{(py)_2C(OH)O\}_4] + 8HNEt_3O_2CMe + 50H_2O \tag{2}$$

Incorporation of N_3^- ions in the $Mn^{II}/MeCO_2^-/(py)_2CO$ reaction system in DMF leads to the remarkable $Mn^{II}_{12}Mn^{III}_{14}$ cluster $[Mn_{26}(DMF)_4(N_3)_{12}O_8(O_2CMe)_6(OH)_4\{(py)_2CO_2\}_{14}]$ (**8**) in 65% yield.[63] Its structure (Figure 3) comprises two symmetry-related Mn_{13} units linked by two 2.200 (end-on) azido ligands to give a dumbbell structure. The $(py)_2CO_2^{2-}$ ligands are of four types (one μ_5, two μ_4, one μ_3), emphasizing the bridging capability of this group. Complex **8** is the largest metal carboxylate cluster containing any form of di-2-pyridyl ketone reported to date. The analogous reaction system with $Me_3CCO_2^-$ instead of $MeCO_2^-$ gives the mixed-valent $Mn^{II}_4Mn^{III}_{20}$ loop $[Mn_{24}(DMF)_4(N_3)_8O_{10}(O_2CCMe_3)_{16}\{(py)_2CO_2\}_{12}]$ (**9**) in 60% yield.[63] The loop, which has a saddle-shaped or closed sinusoidal conformation, can also be described as two Mn_{12} "molecular chains" linked by two 2.1111 (Scheme 10) $(py)_2CO_2^{2-}$ groups. Complexes **8** and **9** have relatively large ground-state spin values (S = 8 and 7, respectively). Both **8** and **9** (in the form of single crystals) show magnetization hysteresis loops below 1.0 and 0.8 K, respectively, confirming that these complexes are SMMs. The U_{eff} value of 46 K for the acetate cluster is the highest yet observed for a $Mn^{II/III}$ mixed-valent complex, although it is still significantly smaller than that for the $[Mn_6(EtOH)_6(Et\text{-}sao)_6O_2\{O_2CPh(Me)_2\}_2]$ complex (86 K).[23]

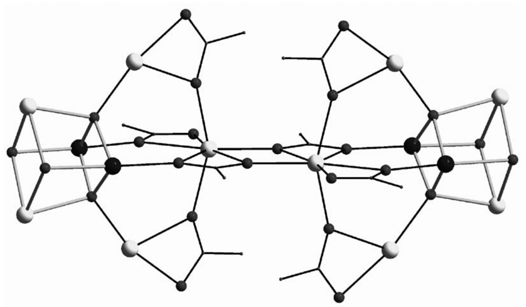


Figure 2. A simplified view of $[Mn^{II}_{10}Mn^{III}_4O_4(O_2CMe)_{20}\{(py)_2C(OH)O\}_4]$ (**7**) emphasizing the cubane $\{Mn^{II}_2Mn^{III}_2(\mu_3\text{-}O)_2(\mu_3\text{-}OR'')_2\}^{4+}$ subcores, which are highlighted.

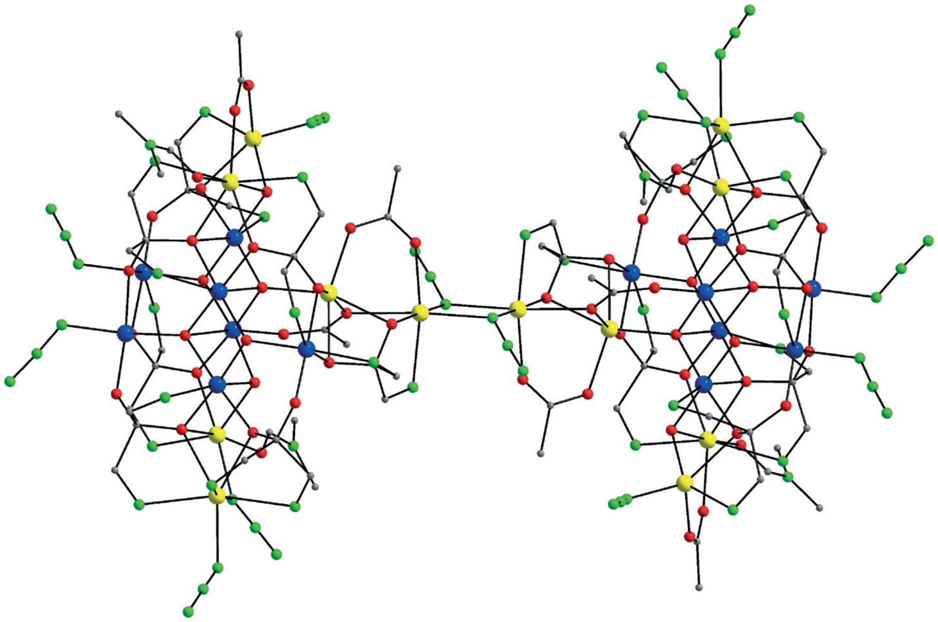


Figure 3. The dumbbell-shaped structure of $[Mn_{26}(DMF)_4(N_3)_{12}O_8(O_2CMe_2)_6(OH)_4\{(py)_2CO_2\}_{14}]$ (**8**). Only the *ipso* C atoms of the $(py)_2CO_2^{2-}$ pyridyl groups are shown. Color code: Mn^{II} yellow, Mn^{III} blue, O red, N green, C gray.

Use of the $(py)_2CO/N(CN)_2^-$ "blend" in manganese(II) acetate chemistry has yielded the neutral, antiferromagnetic cubane $[Mn_4\{N(CN)_2\}_2(O_2CMe)_2\{(py)_2C(OH)O\}_4]$ (**10**).[64] Complex **10** has a structure similar to **6a**, the only difference being the replacement of two monodentate acetato ligands of the latter by two monodentate dicyanamido groups in the former.

The $Mn/PhCO_2^-/(py)_2CO$ reaction system is also fertile. The syntheses, crystal structures and EPR/magnetochemical study have recently been described for $[Mn_3(O_2CPh)_6\{(py)_2CO\}_2]$ (**11**), $[Mn_3(O_2CPh)_6\{(py)_2CO\}_2]\cdot 2MeCN$ (**12**·2MeCN), and $[Mn_4(O_2CPh)_4\{(py)_2C(OH)O\}_4]$ (**13**).[65] Complexes **11** and **12**·2MeCN are linkage isomers. The trinuclear molecules of both complexes have a linear structure, one 2.21 and two *syn,syn* 2.11 $PhCO_2^-$ groups spanning its pair of Mn^{II} ions. The terminal Mn^{II} ions are each capped by one 1.011 (Scheme 5) $(py)_2CO$ ligand in orange **11** and one 1.110 (Scheme 5) $(py)_2CO$ molecule in the yellow isomer **12**·2MeCN. Detailed studies[51a,65] have shown that the 1.110 coordination mode of the $(py)_2CO$ ligand is *kinetically* favorable, while the 1.011 mode is the *thermodynamically* stable ligation mode. The structure of **13**[65] is fairly similar to that of the acetate analogue **6a**.[61b] Complexes **11** and **12**·2MeCN react spontaneously with H_2O and undergo partial oxidation by atmospheric O_2 in MeCN to give a mixture of **13** and the $(py)_2CO$-free $Mn^{II}_4Mn^{III}_2$ cluster $[Mn_6O_2(O_2CPh)_{10}(MeCN)_4]$.[66] Recent results from our group[67] indicate that complex **13** can be oxidized and hydrolyzed under strong conditions, forming the mixed-valent clusters $[Mn^{II}_4Mn^{III}_4(H_2O)_2O_2(O_2CPh)_8\{(py)_2C(OH)O\}_2\{(py)_2CO_2\}_2](ClO_4)_2$ (**14**) and $[Mn^{II}_8Mn^{III}_{10}Mn^{IV}_2(O_2CPh)_{18}\{(py)_2C(OEt)O\}_2\{(py)_2CO_2\}_6](ClO_4)_2$ (**15**), fragments of which are structurally related to **13**. Compound **15** contains two $Mn^{II}_4Mn^{III}_4$ cluster subunits, each of which is structurally similar to **14**.

Somewhat to our surprise, the products from the $Mn/EtCO_2^-/(py)_2CO$ reaction system in alcohols are different as compared with the products from the $Mn/MeCO_2^-/(py)_2CO$ system in alcohols. For example, cluster $[Mn^{II}_2Mn^{III}_6O_2(O_2CEt)_8\{(py)_2C(OMe)O\}_2\{(py)_2CO_2\}_4]$ (**16**),[68] whose core consists of a central "butterfly" $\{Mn^{III}_4(\mu_3\text{-}O)_2\}^{8+}$ subcore bridged to two $\{Mn^{II}Mn^{III}(\mu_2\text{-}OR'')_2\}^{3+}$ units, has no counterpart in manganese acetate chemistry.

We recently reported an extension of the use of $(py)_2CO$ in non-carboxylate Mn chemistry, which yielded $[Mn_{26}(MeOH)_6O_{16}(OMe)_{12}\{(py)_2CO_2\}_{12}](OH)_6$ (**17**) according to Equation (3). Complex **17** is another mixed-valent $Mn^{II}_4Mn^{III}_{22}$ complex, like $[Mn_{26}(N_3)_6O_{16}(OMe)_{12}\{(py)_2CO_2\}_{12}]$ (**18**)[70a] and $[Mn_{26}(H_2O)O_{16}(OH)_2(OMe)_{15}\{(py)_2CO_2\}_{12}](ClO_4)$ (**19**),[70b] previously reported by Kessissoglou's group, and shows both some similarities and differences relative to these previously reported complexes. In fact, interesting comparisons can be made among the three: (i) complex **17** has a different chemical composition from **18** and **19**, illustrating how small changes in the preparative procedures can affect the product identity; (ii) compounds **17**–**19** exhibit slightly different magnetic properties, emphasizing the contribution of the peripheral ligation to the observed magnetic behavior; and (iii) complex **17** has allowed for the first time for this group of $Mn^{II}_4Mn^{III}_{22}$ clusters the observation of hysteresis loops in magnetization vs. applied direct current (dc) magnetic field scans, unequivocally establishing the complex to be an SMM.

$$26Mn^{2+} + 12(py)_2CO + 18MeO^- + 28NEt_3 + 11/2O_2 + 17H_2O \rightarrow [Mn_{26}(MeOH)_6O_{16}(OMe)_{12}\{(py)_2CO_2\}_{12}]^{6+} + 28HNEt_3^+ \qquad (3)$$

The complicated $\{Mn_{26}(\mu_4\text{-}O)_{10}(\mu_3\text{-}O)_6(\mu_3\text{-}OMe)_{12}(\mu_2\text{-}OR'')_{12}\}^{18+}$ core of **17** (Figure 4) consists of an internal Mn^{III}_{16} cage-like unit of adjacent Mn_4 tetrahedra surrounded by an external $Mn^{II}_4Mn^{III}_6$ shell. The latter is held together by the alkoxido arms of twelve 3.2111 (Scheme 10) $(py)_2CO_2^{2-}$ groups. Variable-temperature (1.8–300 K), solid-state dc magnetic susceptibility studies indicate that **17** is predominantly antiferromagnetically coupled with a resulting $S = 6$ ground state, a conclusion confirmed by the in-place alternating current (ac) susceptibility data. The observation of out-of-phase ac susceptibility signals suggests that **17** might be an SMM, and this is confirmed by single-crystal magnetization vs. dc field sweeps that exhibit hysteresis, the diagnostic property of a magnet (Figure 5). Combined out-of-phase ac susceptibility and magnetization decay vs. time data collected below 1.1 K were used to construct an Arrhenius plot; the fit of the thermally activated region above ca. 0.1 K gives $U_{eff} = 30$ K. At lower temperatures, the complex exhibits temperature-independent relaxation, characteristic of ground-state quantum tunneling of magnetization between the lowest-lying $M_S = \pm 6$ levels. Complexes **17**–**19** join only a handful of Mn clusters with a nuclearity of 26[63,69,70] or larger (Mn_{30},[71] Mn_{32},[72] Mn_{40},[73] Mn_{84}[74]). It is interesting that four of the nine Mn_x complexes with $x \geq 26$ contain $(py)_2CO_2^{2-}$ as one of the main bridging/chelating ligands.

The published work in *iron* cluster chemistry with $(py)_2CO$-based ligand comes from our group.[55,75] The great coordinative flexibility and versatility of the $(py)_2CO$-based anionic ligands, and the μ_2 or μ_3 potential of catecholato(–2) ligands, prompted us to combine $(py)_2CO$ with $dbcatH_2$ to aim for new types of Fe^{III} clusters. The loss of a degree of the synthetic control would be more than compensated for by the vast diversity of structures expected using the combination of ligands. Our first efforts along this line were successful, and led to the previously mentioned (part 3.1) tetranuclear complex **4** and to the triangular compound $(HNEt_3)[Fe_3(dbcat)_4\{(py)_2C(OH)O\}_2]$ (**20**).[55] Both complexes are characterized by antiferromagnetic exchange interactions. The presence of two different high-spin Fe^{III} sites with NO_5 and N_2O_4 coordination spheres in **4** is reflected in its variable-temperature ^{57}Fe-Mössbauer spectra which analyze as two quadrupole-split doublets.[55]

The preparation and full study of the enneanuclear Fe^{II} clusters $[Fe_9(O_2CMe)_8\{(py)_2CO_2\}_4(X)_2]$, where $X^- = OH^-$ (**21**), N_3^- (**22**), and OCN^- (**23**), have been reported[75] as a result of our search for Fe SMMs. The azido and isocyanato complexes were prepared by our strategy[59,60,76] involving substitution of bridging hydroxido ligands (in this

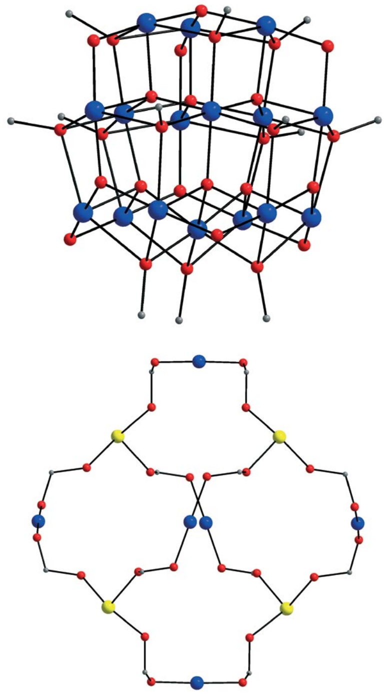


Figure 4. RovRay representation of the internal Mn_{16} unit (top) and the external Mn_{10} shell (bottom) of complex $[Mn_{26}(MeOH)_6O_{16}(OMe)_{12}\{(py)_2CO_2\}_{12}](OH)_6$ (**17**). Color code: Mn^{II} yellow, Mn^{III} blue, O red, C gray.

case the OH^- ion acts as a μ_4 or 4.4 ligand) by end-on azido or isocyanato groups (in this case by 4.400 N_3^- or 4.04 OCN^- ligands). Being strong ferromagnetic couplers, the end-on and *N*-cyanato (isocyanato) ligands are good substitutes for hydroxido bridges in 3d metal clusters to increase the ground-state *S* value.[76] The molecular structures of **21**–**23** consist of eight Fe^{II} ions that form two slightly staggered parallel squares, with a ninth eight-coordinate Fe^{II} center located between them. The four $(py)_2CO_2^{2-}$ ligands adopt the 5.3311 coordination mode (Scheme 10). The molecular structure of the representative compound **23** is shown in Figure 6. As indicated by dc magnetic susceptibility techniques, the substitution of N_3^- or OCN^- for OH^- induces strong ferromagnetic couplings in **22** and **23**, leading to higher ground-state spins relative to the spin of **21**. Magnetization experiments have shown that the ground state of **22** or **23** is not well isolated from excited states, and as a result it cannot be unambiguously determined. Studies by ac susceptometry have revealed out-of-phase signals, which suggests that the azido and isocyanato clusters exhibit a slow relaxation of magnetization that follows Arrhenius behavior, typical for SMMs, with energy barriers of 41 K for **22** and 44 K for **23**. Slow magnetic relaxation is also observed by using zero-field ^{57}Fe-Mössbauer spectroscopy. Characteristic integer-spin EPR signals are observed at the X-band for **21**, whereas **22** and **23** are EPR-silent at this frequency. ^{1}H NMR spectrometry in CD_3CN reveals that the three complexes are stable in solution.

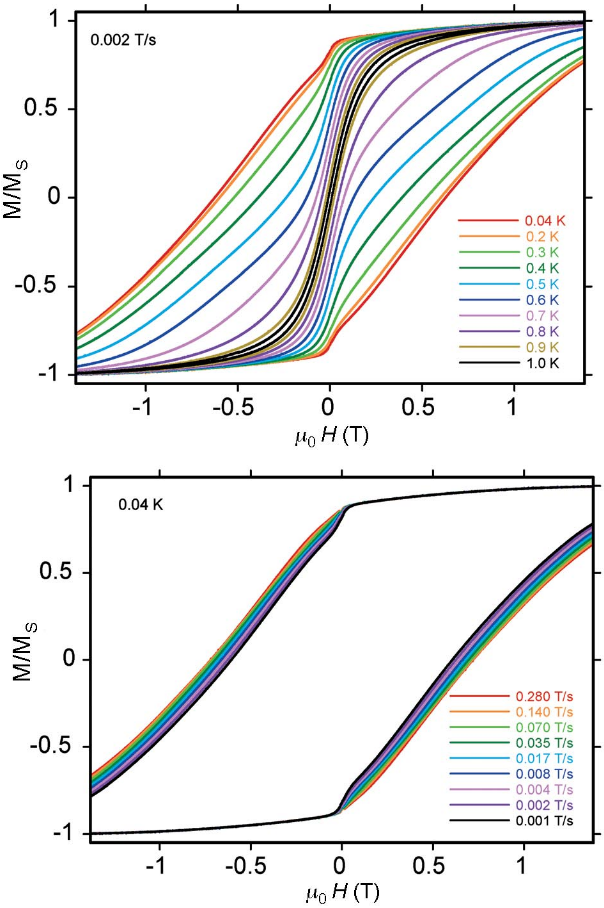


Figure 5. Magnetization (*M*) vs. dc field hysteresis loops for a single crystal of $[Mn_{26}(MeOH)_6O_{16}(OMe)_{12}\{(py)_2CO_2\}_{12}](OH)_6$ (**17**) at the indicated temperatures and a fixed field sweep rate of 0.002 T/s (top) and at the indicated field sweep rates and a fixed temperature of 0.04 K (bottom). The magnetization is normalized to its saturation value, M_S.

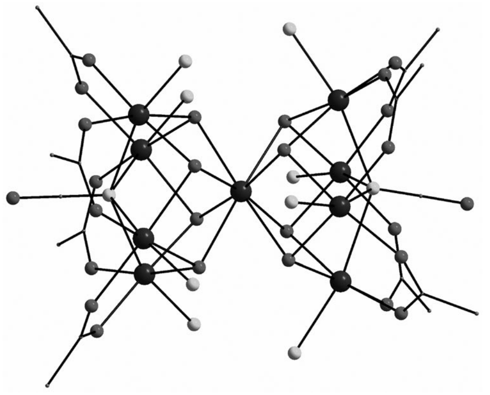


Figure 6. The structure of $[Fe_9(O_2CMe)_8(OCN)_2\{(py)_2CO_2\}_4]$ (**23**). All noncoordinated atoms of the $(py)_2CO_2^{2-}$ ligands have been omitted for clarity.

Following the work on *cobalt* cluster chemistry with $(py)_2CO$-based ligands in late 1990s and early in this millennium,[58,60,77,78] relatively little has been reported in the last seven years. Work from other groups involves the cubane clusters $[Co_4(H_2O)(O_2CMe)_3\{(py)_2C(OH)O\}_4](ClO_4)$ (**24**)[62b] and $[Co_4(O_2CMe)_4\{(py)_2C(OH)O\}_4]\cdot 7H_2O$

(**25**·7H$_2$O).[79] By contrast with **24**[62b] and the monohydrate cluster $[Co_4(O_2CMe)_4\{(py)_2C(OH)O\}_4]\cdot H_2O$ (**26**·H$_2$O),[58] which are characterized by intramolecular ferromagnetic exchange interactions, compound **25** was reported to be antiferromagnetically coupled;[79] the reasons for this difference are not clear. The cubane cluster $[Co_4\{N(CN)_2\}_2(O_2CMe)_2\{(py)_2C(OH)O\}_4]$ (**27**) prepared by our group is also ferromagnetic.[64]

The reaction of $Co(O_2CPh)_2$ with $(py)_2CO$ and NaN_3 in DMF allows isolation of the Co^{II}_4 cluster $[Co_4(N_3)_2(O_2CPh)_2\{(py)_2C(OH)O\}_4]$ (**28**)[80] instead of the designed benzoate analogue of the enneanuclear acetate cage $[Co^{II}_9(N_3)_2(O_2CMe)_8\{(py)_2CO_2\}_4]$ (**29**).[60] X-ray diffraction analysis reveals a defective double-cubane core (Figure 7) in which the Co^{II} ions are linked by 2.200 azido groups and two kinds of O bridges. Two $(py)_2C(OH)O^-$ ions adopt the 3.3011 coordination mode and the other two bind in the 2.2011 mode (see Scheme 9). Studies of dc magnetic susceptibility on **28** in the 2.0–300 K range indicate bulk ferromagnetic coupling. Complex **28** is structurally related to the azido-containing complexes $[Co_4(2.200\text{-}N_3)_2(1.100\text{-}N_3)_2\{(py)_2C(OH)O\}_2\{(py)_2C(OMe)O\}_2]$ (**30**)[78] and $[Co_4(H_2O)_2(2.200\text{-}N_3)_2\{(py)_2C(OH)O\}_2\{(py)_2C(OMe)O\}_2](BF_4)_2$ (**31**).[77b] All three complexes have a defective, double-cubane motif. There are two chemical differences along the series, which have no structural effect. First, complexes **30** and **31** have two $(py)_2C(OH)O^-$ and two $(py)_2C(OMe)O^-$ ligands; this is a consequence of the presence of MeOH that leads to $(py)_2C(OMe)O^-$ ligands. Second, the two terminal monodentate ligands differ in the three complexes; these are $PhCO_2^-$ ions in **28**, N_3^- groups in **30**, and H$_2$O molecules in **31** (giving rise to a cationic species). The presence of $PhCO_2^-$ groups in **28** is a result of the high $PhCO_2^-/N_3^-$ ratio (4:1) used,[80] whereas the presence of two terminal azido ligands in **30** can be explained by the lower $MeCO_2^-/N_3^-$ ratios (2:1, 1:1, 1:1.5, 1:2) in the reaction mixtures.[78] The existence of aqua ligands in the structure of **31** is certainly due to the presence of BF_4^- ions in the reaction system; the latter favor the formation of cationic species. As expected from the similar core with **28**, the Co^{II}···Co^{II} exchange interactions in **30** and **31** are ferromagnetic in nature.

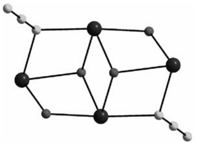


Figure 7. The defective, double-cubane core present in complex $[Co_4(N_3)_2(O_2CPh)_2\{(py)_2C(OH)O\}_4]$ (**28**).

Structurally and magnetically interesting *nickel* clusters with $(py)_2CO$-based ligands, published before 2002, are $[Ni_9(N_3)_2(O_2CMe)_8\{(py)_2CO_2\}_4]$ (**32**, $S = 9$),[59] $[Ni_4(2.200\text{-}N_3)_2(1.100\text{-}N_3)_2\{(py)_2C(OH)O\}_4]$ (**33**, $S = 4$),[81] and $[Ni_4(H_2O)_2(2.200\text{-}N_3)_2\{(py)_2C(OH)O\}_2\{(py)_2C(OMe)O\}_2](ClO_4)_2$ (**34**, $S = 4$).[56d] Complex **32** has a structure almost identical with the Fe$^{II[75]}$ and Co$^{II[60]}$ analogues, while the cation of **34** is structurally similar to the cation of **31**.[77b] Complex **33** is structurally related to the defective, double-cubane Co$^{II}_4$ cluster **28**,[80] the only differences being the different metal ions and the replacement of the two monodentate $PhCO_2^-$ ligands in the latter by two extra terminal azido groups in the former.

The recently reported research in this area is dominated by cubane and defective double-cubane clusters. Complexes $[Ni_4(H_2O)_2(O_2CMe)_2\{(py)_2C(OH)O\}_4](ClO_4)_2$ (**35**),[53b] $[Ni_4(O_2CMe)_3\{(py)_2C(OH)O\}_4](ClO_4)$ (**36**),[53b] $[Ni_4(O_2CMe)_3\{(py)_2C(OH)O\}_4](O_2CMe)$ (**37**),[53b] $[Ni_4\{N(CN)_2\}_2(O_2CMe)_2\{(py)_2C(OH)O\}_4]$ (**38**),[64] $[Ni_4\{(py)_2C(OH)O\}_4(SO_4)_2]$ (**39**),[82] and $[Ni_4(H_2O)_4\{(py)_2C(OH)O\}_4](ClO_4)_4$ (**40**)[83] are cubanes with variable magnetic behavior, whereas $[Ni_4(O_2CMe)_4\{(py)_2C(OH)O\}_4]$(**41**)[53b] and $[Ni_4(CH_3CONHO)_2\{(py)_2C(OEt)O\}_2\{(py)_2C(OH)O\}_2]Cl_2$ (**42**)[84] are defective double cubanes.

Reactions of $(py)_2CO$ and excess Ni^{II} carboxylates in MeCN/H$_2$O under strongly basic conditions yield the carboxylate clusters $[Ni_{11}(H_2O)_2(O_2CMe)_{12}(OH)_6\{(py)_2C(OH)O\}_4]$(**43**) and $[Ni_5(H_2O)(MeCN)(O_2CPh)_6(OH)_2\{(py)_2C(OH)O\}_2]$ (**44**).[85] The formation of the acetate cluster is summarized in Equation (4); the cluster contains the novel $\{Ni_{11}(\mu_3\text{-}O_{carboxylato})_2(\mu_3\text{-}O_{hydroxido})_6(\mu_3\text{-}O_{(py)2C(OH)O-})_4\}^{10+}$ core (Figure 8) consisting of two cubane Ni$^{II}_4$ subunits that are bridged by a nonlinear Ni$^{II}_3$ moiety through acetato and hydroxido ligands. A unique structural feature of **43** is the novel 4.31 ligation mode adopted by the two $MeCO_2^-$ groups that participate in the formation of the two cubane subunits. The magnetic study of **43** and **44** is in progress.

$$11Ni(O_2CMe)_2\cdot 4H_2O + 4(py)_2CO + 10NEt_3 \rightarrow [Ni_{11}(H_2O)_2(O_2CMe)_{12}(OH)_6\{(py)_2C(OH)O\}_4] + 10(HNEt_3)(O_2CMe) + 32H_2O \quad (4)$$

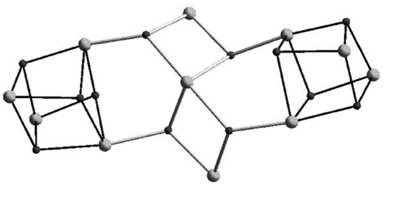


Figure 8. The $\{Ni_{11}(\mu_3\text{-}O_{carboxylato})_2(\mu_3\text{-}O_{hydroxido})_6(\mu_3\text{-}O_{(py)2C(OH)O-})_4\}^{10+}$ core present in **43**.

The highest nuclearity *copper*/$(py)_2CO$ clusters reported before 2002 are $[Cu_8(O_2CMe)_4\{(py)_2C(OH)O\}_8](ClO_4)_4$ (**45**),[53e,86] $[Cu_7(O_2CMe)_6(OH)_2\{(py)_2CO_2\}_3]$ (**46**),[57] $[Cu_{12}(O_2CMe)_{12}\{(py)_2CO_2\}_6]$ (**47**), and $[Cu_8L_4(O_2CMe)_4\{(py)_2CO_2\}_4]$ (**48**),[56e] where L is 2-hydroxypyridine; complexes **47** and **48** have novel fly- and paddle-wheel-like structures. More recent work from other groups involves the cubane cluster $[Cu_4(ClO_4)_2(H_2O)_2\{(py)_2C(OH)O\}_4]$ (**49**)[83] and the structurally impressive, undecanuclear cage $[Cu_{11}(O_2CMe)_{12}\{(py)_2CO_2\}_5]$ (**50**).[87] The $(py)_2CO_2^{2-}$ groups in the latter adopt the 3.2211 and 4.2211 coordination modes (see Scheme 10). The central Cu$^{II}_7$ subunit of this cluster has a vertex-sharing, double tetrahedral metal topology and is structurally similar to the discrete compound **46**.

Since the ternary $(py)_2CO/RCO_2^-/N_3^-$ (R = H, Me, Me_3C, Ph,...) ligand combination ("blend") is an efficient means to high-nuclearity Mn,[63] Fe,[75] Co,[60,80] and Ni[59] complexes, including SMMs,[63,75] we decided to extend the exploration of this general ligand combination in Cu^{II} chemistry. We have just reported[88] that the $Cu^{II}/(py)_2CO/PhCO_2^-/N_3^-$ reaction system provides access to the antiferromagnetic (S = 0) cluster $[Cu_6(N_3)_2(O_2CPh)_4\{(py)_2C(OH)O\}_2\{(py)_2CO_2\}_2]$ (**51**). The novel core (Figure 9) consists of four square-pyramidal Cu^{II} ions located at four alternate vertices of a central defective cubane unit (a cubane missing two opposite edges), two μ_3-O atoms from the 3.3011 $(py)_2C(OH)O^-$ groups, and two μ_2-O atoms from two different 4.2211 $(py)_2CO_2^{2-}$ ligands (these four O atoms occupy the remaining vertices of the cube), two additional satellite Cu^{II} ions across the missing edges, and two μ_2-O atoms that belong to the two different $(py)_2CO_2^{2-}$ groups, and each links the cubane unit with a satellite metal ion.

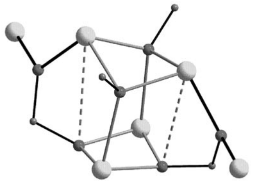


Figure 9. The $\{Cu^{II}_6(\mu_3\text{-}OR'')_2(\mu_2\text{-}OR'')_4\}^{6+}$ core of $[Cu_6(N_3)_2(O_2CPh)_4\{(py)_2C(OH)O\}_2\{(py)_2CO_2\}_2]$ (**51**), emphasizing the central defective cubane subcore (thick gray lines). The gray dashed lines represent the two missing edges of the cubane unit.

In an attempt to study spin frustration phenomena,[89] we have just prepared and structurally characterized[85] a family of noncentered, triangular clusters with the general formula $[Cu_3\{(py)_2C(OR')O\}_3(solvent)_x](ClO_4)_3$ [R′ = Me, solvent = H_2O, x = 1, **52**; R′ = Et, solvent = EtOH, x = 3, **53**; R′ = Et, solvent = MeCN, x = 3, **54**]; the $(py)_2C(OR')O^-$ ions act as 2.2011 ligands (see Scheme 9).

Most *zinc* complexes of $(py)_2CO$-based ligands are mononuclear[51e,53i] or dinuclear.[53i,90] The highest nuclearity cluster, $[Zn_6(H_2O)_2(O_2CMe)_8\{(py)_2CO\}_2]$ (**55**), was reported by our group in 2001.[91] The cluster was prepared by a "depolymerization" approach,[91] which involves the cleavage, in a controlled manner, of the 3D polymer ("polymer of clusters") $[Zn_6(O_2CMe)_8\{(py)_2CO\}_2]_n$ (**56**) containing recognizable Zn^{II}_6 units. The use of the $(py)_2CO/NO_3^-$ and $(py)_2CO/SO_4^{2-}$ "blends" in Zn chemistry yields the cubane clusters $[Zn_4(H_2O)(NO_3)_3\{(py)_2C(OH)O\}_4](NO_3)$ (**57**)[90] and $[Zn_4(H_2O)_2\{(py)_2C(OH)O\}_4(SO_4)_2]$ (**58**),[82] respectively; the nitrate and sulfate ions behave as monodentate ligands. The main interest in such Zn^{II} clusters arises from their luminescent properties. Upon excitation at 371 nm, complex **57** displays blue photoluminescence in the solid state at room temperature with two emission maxima at 430 and 455 nm (Figure 10).[90] The structurally analogous cluster $[Zn_4(H_2O)_2(O_2CMe)_2\{(py)_2C(OH)O\}_4](ClO_4)_2$ (**59**) exhibits rather similar behavior in the solid state (at both ambient and cryogenic temperatures), displaying two emission maxima at approximately 430 and 475 nm upon excitation at 325 nm.[62b] The emission of the clusters is mainly due to the fluorescence from the intraligand excited state.

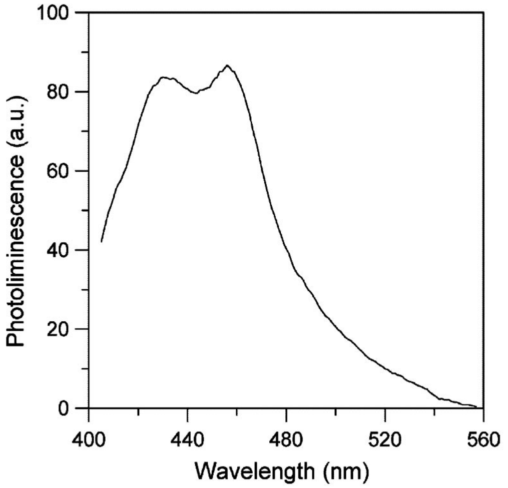


Figure 10. Solid-state photoluminescence spectrum of complex $[Zn_4(H_2O)(NO_3)_3\{(py)_2C(OH)O\}_4](NO_3)$ (**57**) with excitation at 371 nm.

A few years ago, Polarz and co-workers reported on the intriguing properties of the cubane $Zn_4\{(py)_2C(OH)O\}_4(O_2CMe)_{4-x}(ClO_4)_x$ and heterocubane $Zn_{4-y}M^{II}_y\{(py)_2C(OH)O\}_4(O_2CMe)_{4-x}(ClO_4)_x$ molecular clusters (M = Mn, Co, Ni) and their exploitation for the preparation of metal-doped 3d metal oxides.[92] They showed that (i) the homometallic Zn^{II} cluster is a single-source precursor for nanoscaled ZnO; (ii) any combination and permutation of bimetallic clusters are easily accessible, and (iii) these bimetallic clusters can be used to prepare nanoscaled bimetallic oxides. Multimetallic oxides have been known in solid-state chemistry for a long time, but the high processing temperatures typically applied make them less suitable for the synthesis of nanoscaled materials.[93] In this respect, the use of molecular single-source precursors can solve this problem by the creation of molecular building blocks suitable for bottom-up formation of oxides (or other materials).

The coordination chemistry of $(py)_2CO$ with *cadmium* is a less explored area. The dinuclear complex $[Cd_2(\mu_2\text{-}Br)_2Br_2\{(py)_2C(OH)_2\}_2]$ (**60**)[94] and the cubane clusters $[Cd_4(O_2CMe)_3\{(py)_2C(OH)O\}_4](ClO_4)$(**61**),[62b]$[Cd_4(NCS)_4\{(py)_2C(OH)O\}_4]$ (**62**),[95a] and $[Cd_4(\eta^2\text{-}FcCOO)_3(\eta^1\text{-}FcCOO)_3\{(py)_2C(OH)O\}_4]$ (**63**),[95b] where Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$, have been structurally characterized. In compound **63**, three ferrocenecarboxylate groups behave as chelating ligands, and one acts as a monodentate ligand, which results in 7- and 6-coordination at the Cd^{II} sites. Complexes **61** and **63** display blue and green photoluminescence, respectively, in the solid state.

Surprisingly, $(py)_2CO$-based ligands had been completely ignored in *lanthanide* chemistry before 2006. In that year, we reported on the preparation and physical/spectroscopic characterization of several mono- and dinuclear Ln^{III} complexes of such ligands. The structures of $[Er(NCS)_3\{(py)_2$-

$C(OEt)(OH)\}_3]$ (**1**),[53a] $[Er_2(MeOH)(NCS)_3\{(py)_2C(OEt)(OH)\}_3]$ (**64**),[53a] and $[Er_2(NO_3)_3\{(py)_2C(OH)O\}\{(py)_2C(OMe)O\}_2]$ (**65**)[96] have been solved by single-crystal X-ray crystallography. In complex **64**, the two Er^{III} ions are triply bridged by the deprotonated O atoms of the 2.2011 $(py)_2C(OMe)O^-$ ligands (Scheme 9). The coordination polyhedra of both Er^{III} ions are best described as distorted dodecahedra. The two Er^{III} ions in **65** (Figure 11) are doubly bridged by the deprotonated O atoms of the 2.201_11_1 (Scheme 9) $(py)_2C(OH)O^-$ ligand and one 2.2011 $(py)_2C(OMe)O^-$ group. One Er^{III} ion is in a nine-coordinate, tricapped trigonal-prismatic ligand environment, while the other is in an eight-coordinate, dodecahedral environment. The Eu^{III} and Tb^{III} analogues of **65** display intense red and green emissions, respectively, in the solid state at room temperature; this photoluminescence is achieved by an indirect process (antenna effect).[96] The crystal structures of the Pr^{III}, Sm^{III}, and Gd^{III} analogues of **1** have just been reported.[97]

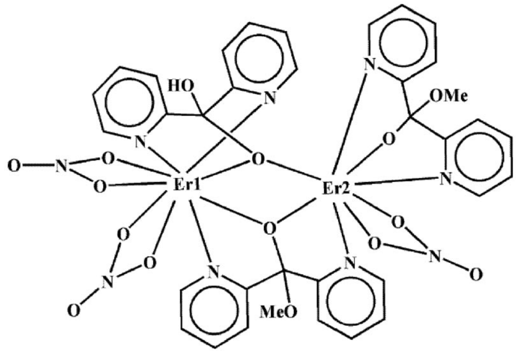


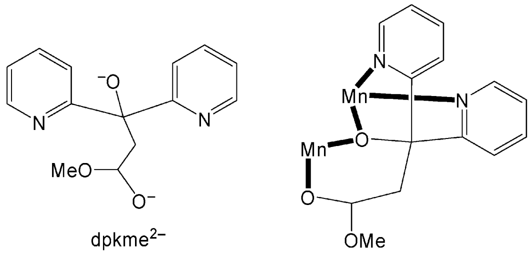
Figure 11. A schematic picture of the molecular structure of $[Er_2(NO_3)_3\{(py)_2C(OH)O\}\{(py)_2C(OMe)O\}_2]$ (**65**).

Complexes of $(py)_2CO$ and its derivatives with main-group metals are rare. An exception is *bismuth*. Complex $[Bi_2(O_2CCF_3)_4\{(py)_2C(OH)O\}_2(THF)_2]$ (**67**)[56b] is obtained by the reaction of $BiPh_3$ with $(py)_2CO$ in the presence of CF_3CO_2H in tetrahydrofuran (THF). The novel cluster $[Bi_5(MeCN)\{(py)_2CO_2\}_6](ClO_4)_3$ (**67**) is synthesized by the reaction of the oxido/hydroxido precursor $[Bi_9(\mu_3\text{-}O)_8(\mu_3\text{-}OH)_6](ClO_4)_5$ and $(py)_2CO$. The cation of **67** can be described as a tetrahedral assembly of four, trigonal-antiprismatic Bi^{III} ions arranged around a single endohedral, tricapped trigonal-prismatic Bi^{III} center.[98] The $(py)_2CO_2{}^{2-}$ groups of this cluster adopt the 3.2211 and 3.2111 ligation modes (see Scheme 10).

3.3. Use of $(py)_2CO$ for the Preparation of Coordination Polymers

Despite their bridging behavior, the anionic $(py)_2CO$-based ligands form only a limited number of coordination polymers; in many of them the polymerization is achieved through other bridging ligands present in the complexes, the $(py)_2CO$-type ligand serving to stabilize the dinuclear or cluster repeating unit.

The most remarkable metal polymer bearing a $(py)_2CO$-type ligand is the *manganese* compound $[Mn_6(dpkme)_2(MeOH)_2(N_3)_4(O_2CMe)_2\{(py)_2CO_2\}_2]_n$ (**68**),[99] where $dpkme^{2-}$ is the dianion of a new form of $(py)_2CO$ (Scheme 11). The dark red complex is prepared by the reaction of $Mn(ClO_4)_2{\cdot}6H_2O$, $(py)_2CO$, $NaO_2CMe{\cdot}3H_2O$, NaN_3, and NEt_3 in a 1:1:2:1:1 molar ratio in MeOH. Compound **68** is a 1D chain (Figure 12) containing a mixed-valent $Mn^{II}{}_4Mn^{III}{}_2$ repeating unit that consists of a central, planar $\{Mn^{II}{}_2Mn^{III}{}_2\}$ rhombus, which is additionally linked to two extrinsic Mn^{II} ions. End-on azido groups bridge the Mn_6 unit to its neighbors on either side to form the chain; the $(py)_2CO_2{}^{2-}$ groups bind in the 4.2211 mode (Scheme 10). The shortest Mn···Mn separations between chains are all greater than 10 Å, and there are no significant interchain H-bonding or π–π stacking interactions.



Scheme 11. The ligand $dpkme^{2-}$ that is present in complex $[Mn_6(dpkme)_2(MeOH)_2(N_3)_4(O_2CMe)_2\{(py)_2CO_2\}_2]_n$ (**68**) (left); this ligand is a transformation product of $(py)_2CO$. The coordination mode of $dpkme^{2-}$ in **68** (right).

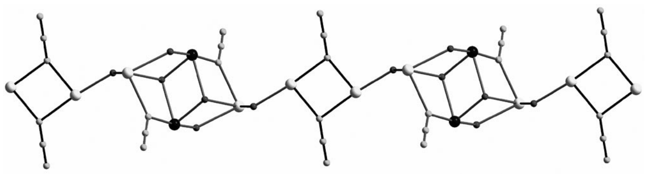


Figure 12. Section of the 1D chain of $[Mn_6(dpkme)_2(MeOH)_2(N_3)_4(O_2CMe)_2\{(py)_2CO_2\}_2]_n$ (**68**).

The Mn_6 repeating unit has an $S = 4$ ground state, and this is as expected for a ferromagnetically coupled central rhombus with a resulting $S = 9$ spin and antiferromagnetic coupling between it and the two "extrinsic" Mn^{II} ions. Studies of ac susceptibility and magnetization reveal that **68** is a single-chain magnet (SCM).[99] SCMs are 1D metal-containing polymers that possess a large uniaxial anisotropy, strong intrachain exchange interactions without spin compensation between the high-spin magnetic units, and good isolation of the chains in order to avoid 2D or 3D ordering.[24,100] The number of SCMs is still relatively small even though the first one was discovered almost ten years ago.[101] Of the currently known examples, the majority are heterospin systems containing at least two different spin carriers and obtained by a direct approach using SMMs as building blocks.[24] Homospin SCMs, like **68**, are rare, and many of them have been synthesized by a self-assembly approach from highly anisotropic metal sources, such as

Mn^{III}, $Fe^{II/III}$, and Co^{II} ions.[99] It should be noted that **68**[99] and the discrete Mn_{26} compound **8**[63] are made by very similar reactions differing only in the identity of the solvent. In addition, their structures are also related, both involving a Mn_x bridged by end-on azido groups, but differ in that **68** is a chain whereas the Mn_{26} complex is a dumbbell-shaped dimer of clusters.

Three of the reported coordination polymers with anionic $(py)_2CO$-based ligands are *copper* complexes. Work from other groups involves complexes $[Cu_2(N_3)_3\{(py)_2C(OMe)O\}]_n$ (**69**, 1D)[102] with alternating double end-on azido and mixed end-on azido/alkoxido bridges, $[Cu_2Cl_3\{(py)_2C(OMe)O\}]_n$ (**70**, 1D),[56c] which is structurally similar to **69** but has chloride (instead of azido) bridges, and its polymorph formulated as $[Cu_4Cl_6\{(py)_2C(OMe)O\}_2]_n$ (**71**).[103] The polycrystalline, X-band EPR spectrum of **71** at 4.1 K shows an intense broad signal spread over 2900 G with $g = 2.34$, indicative of a bulk concentration of Cu^{II} ions having strong ferromagnetic interactions.[103] There are two 1D Cu^{II} polymers, namely $[CuCl_2\{(py)_2CO\}]_n$ (**72**)[104] and $[Cu(NO_3)_2\{(py)_2CO\}]_n$ (**73**),[56c] in which the ligand retains its carbonyl function and binds in the 1.011 mode (Scheme 5). The 1D structures form through double μ_2-chlorido ligands in the former and one bidentate bridging nitrate group in the latter.

Surprisingly, a plethora of *silver*/$(py)_2CO$ polymeric complexes have been structurally characterized. Earlier examples involve the zigzag chains $[Ag(NO_3)\{(py)_2CO\}]_n$ (**74**) [105a] and $\{[Ag\{(py)_2CO\}](BF_4)\}_n$ (**75**),[105a] in which the ligand adopts the 2.011 and 2.211 coordination modes (Scheme 5), respectively. The Ag^I centers attain distorted tetrahedral (**74**) and square planar (**75**) coordination environments. Incorporation of the noncoordinating BF_4^- anion appears to enhance the opportunity of coordination for the carbonyl group of $(py)_2CO$. Chen, Mak, and coworkers carried out an interesting structural investigation of the complexes derived from the general reaction system $Ag^I/(py)_2CO/X^-$ ($X^- = NO_2^-$, ClO_3^-, ClO_4^-, PF_6^-) and showed that both the anion coordination and π–π stacking interaction play important roles in the solid-state structures of the products.[106] The 1:1 complexes $[Ag(NO_2)\{(py)_2CO\}]_n$ (**76**), $[Ag(ClO_3)\{(py)_2CO\}]_n$ (**77**), $\{[Ag\{(py)_2CO\}](PF_6)\}_n$ (**78**), and $\{[Ag_2(ClO_4)\{(py)_2CO\}_2](ClO_4)\}_n$ (**79**) exhibit three kinds of helical structures, and structural variations within the series result from the different coordination modes of the inorganic anions. The $(py)_2CO$ molecule binds in the 2.011 mode in **76** and **77**, and as a 2.211 ligand in **78**; both the 2.111 and 2.211 ligation modes of $(py)_2CO$ (Scheme 5) are observed in **79**. In the 1:2 complexes $[Ag(ClO_3)\{(py)_2CO\}_2]$ (**80**) and $[Ag(ClO_4)\{(py)_2CO\}_2]$ (**81**), each $(py)_2CO$ ligand coordinates to the Ag^I center through one of its 2-pyridyl groups in an extremely rare monodentate mode (1.010, Scheme 5); the two mononuclear complexes are stabilized by intramolecular π–π stacking interactions and aligned into chains through intermolecular π–π stacking interactions in a zipper-like fashion. In compounds **74**–**79** the polymerization is achieved solely through the bridging $(py)_2CO$ ligand.

We have prepared and characterized a large number of *zinc*- and *cadmium*-containing coordination polymers with $(py)_2CO$-derived ligands, including the above-mentioned (part 3.2) 3D compound **56**,[91] most of which exhibit photoluminescence.[107]

Repeating the reaction that gave the Cu^{II}_6 cluster **51** but simply changing the solvent from MeCN to MeOH produces a mixture of the 1D $[Cu_4(N_3)_4(O_2CPh)_2\{(py)_2C(OMe)O\}_2]_n$ (**82**) and 2D $[Cu_2(N_3)_2(O_2CPh)\{(py)_2C(OMe)O\}]_n$ (**83**) polymers.[88] Mainly because of their identical $Cu^{II}/N_3^-/PhCO_2^-/(py)_2C(OMe)O^-$ (2:2:1:1) ratio, the two complexes can not be isolated separately. The dinuclear units of **83** assemble with two end-on (2.200) azido ligands to form a tetranuclear unit (Figure 13, top). The latter are linked through four end-to-end (2.101) azido ligands to form a 2D layer along the (1 0 –1) plane (Figure 13, middle). The 2D layer adopts the "herringbone" or "parquet floor" architecture, in which each tetranuclear unit serves as two fused 3-connected nodes that self-assemble to create this architecture (Figure 13, bottom).

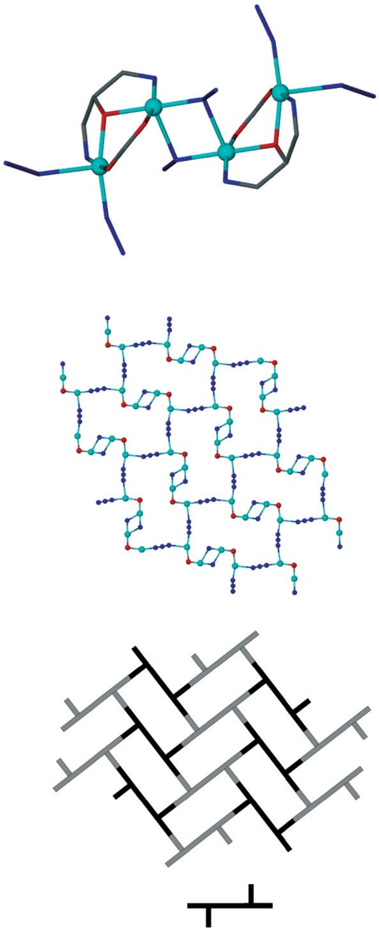


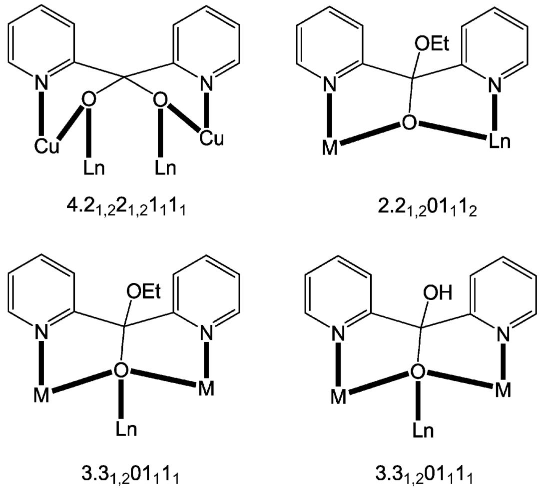
Figure 13. The assembly of two dinuclear units of **83** (top), the 2D layer running along the (1 0 –1) plane (middle) and the herringbone architecture of the same complex based on the tetranuclear units that serve as two fused 3-connected nodes (bottom). Color code: Cu^{II} sky blue, O red, N dark blue, C gray.

The 1D polymers $[Cu_2Cl_3\{(py)_2C(OMe)O\}]_n$ (**84**), $[Cu_2Br_3\{(py)_2(OH)O\}]_n$ (**85**), and $[Cu_8(N_3)_6(O_2CMe)_2\{(py)_2CO_2\}_4]_n$ (**86**) were structurally characterized recently,[108] and they were magnetically characterized at the time of submission of this Microreview. Complex **84** is the $(py)_2C(OH)O^-$ analogue of **70**.[56c] Preliminary data reveal ferromagnetic behavior for **85** and **86**.

3.4. Mixed 3d/4f Metal Complexes Containing $(py)_2CO$-Based Ligands

Mixed transition-metal/lanthanide(III) compounds are of great relevance to the field of molecular magnetism. In the early 1990s, 3d/4f metal cluster chemistry was primarily focused on Gd^{III}-Cu^{II} complexes, notably by Kahn and co-workers, in the desire of understanding the magnetic interactions between two different metal ions.[109] Restricting further discussion to the area of single-molecule magnetism, since the discovery of the $[Mn_{12}O_{12}(O_2CR)_6(H_2O)_x]$ family of SMMs in 1993, a great number of such complexes have been revealed, many of them being Mn clusters containing at least some Mn^{III} centers.[11] On the contrary, heterometallic transition-metal/lanthanide SMMs have not been investigated as much.[11c] The advantages of using Ln^{III} ions in the synthesis of new SMMs are that these ions can provide both large spin (e.g. 7/2 for Gd^{3+}) and considerable single-ion anisotropy. These properties could help to generate SMMs with properties different from those of homometallic, 3d-metal SMMs. We have recently joined ongoing efforts in this subarea[110] and have focused to date primarily on Co^{II}- and Ni^{II}-containing species. We have been employing two general synthetic approaches. The first is the "metal complexes as ligands strategy".[111] We use mononuclear or dinuclear 3d metal complexes with uncoordinated O donor groups; such complexes can be considered as "ligands" and further react with the oxophilic Ln^{III} ions.[112] The second approach is based on "one-pot" procedures and requires a mixture of appropriate 3d- and 4f-metal salts and a carefully chosen ligand featuring distinct coordination compartments for preferential binding of the transition-metal ion and the lanthanide.[112]

Di-2-pyridyl ketone and its derivatives have been little used in the synthesis of 3d/4f metal clusters. The only published report on this topic comes from Li and co-workers, who have prepared the isostructural complexes $[Cu_6Ln_2Cl_2(H_2O)_4(OTf)_2\{(py)_2C(OH)O\}_2\{(py)_2CO_2\}_5](OTf)_2$ (Ln = Eu, **87**; Ln = Gd, **88**; OTf^- is the triflate anion) by solvothermal techniques in MeOH/EtOH.[87] The cation is held together by two 2.2011 $(py)_2C(OH)O^-$ groups (Scheme 9), which bridge two Cu^{II} ions and five 4.2211 $(py)_2CO_2^{2-}$ ligands, each bridging two Cu^{II} and two Ln^{III} centers (Scheme 12). As expected from the hard soft acids and bases (HSAB) principle, the $(py)_2CO_2^{2-}$ donor sites to Ln^{III} are the "hard" deprotonated O atoms. At the center of the cluster cation is located the pair of Ln^{III} ions capped on either side by a triangular array of three Cu^{II} ions. Preliminary variable-temperature magnetic susceptibility data on **88** reveal overall weak antiferromagnetic behavior.[87] Since there are three types of possible exchange interactions, i.e., Cu···Cu, Gd···Gd, and Cu···Gd, a more detailed analysis is difficult.



Scheme 12. The crystallographically confirmed coordination modes of the $(py)_2CO$ derivatives that bridge 3d and 4f metal ions and the Harris notations[3] that describe these modes; M = 3d metal.

We have been using, among others, the mononuclear octahedral complex $[Ni(O_2CMe)\{(py)_2CO\}\{(py)_2C(OH)_2\}](ClO_4)$ (**89**, Figure 14) as a "metalloligand" for the preparation of 3d/4f metal clusters. The Ni^{II} atom is coordinated by one monodentate $MeCO_2^-$, one tridentate chelating $(py)_2C(OH)_2$ molecule (1.1011), and one bidentate *N*,*N'*-chelating $(py)_2CO$ ligand (1.011). There are three free O atoms available for coordination to Ln^{III} ions. The reactions of this precursor (which can be considered as the "ligand") with $Ln(NO_3)_3\cdot xH_2O$ (the "metal ion") give indeed heterometallic clusters. However, the identity of the precursor differs significantly in the products (vide infra), and we thus prefer the term "pseudo metal complexes as ligands" for this approach.

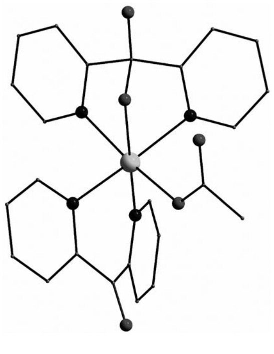


Figure 14. The mononuclear cation $[Ni(O_2CMe)\{(py)_2CO\}\{(py)_2C(OH)_2\}]^+$, which is present in precursor complex **89**.

The reactions of **89** with lanthanide(III) nitrates in EtOH give ionic complexes with the general formula $[LnNi_2(H_2O)(NO_3)\{(py)_2C(OEt)O\}_4]_2[Ln(NO_3)_5](ClO_4)_2$ containing the 10-coordinate pentanitratolanthanidate dianion, ClO_4^- anions, and heterometallic, trinuclear cations with a defective cubane topology, according to the balanced Equation (5). We have structurally characterized[113] the Ln = Gd (**90**), Tb (**91**), and Dy (**92**) members of this family, as well as the analogous Y^{III} (**93**) cluster. The molecular structure and the core of the Ni_2Tb cation of complex **91** are shown in Figure 15. The $(py)_2C(OEt)O^-$ ligands adopt the three coordination modes 2.2011 (Scheme 9), $2.2_{1,2}01_1 1_2$ (Scheme 12), and $3.3_{1,2}01_1 1_1$ (Scheme 12). Expansion of this chemistry on Co^{II} gives a family of isostructural complexes, e.g. $[Co_2Tb(H_2O)(NO_3)\{(py)_2C(OEt)O\}_4]_2[Tb(NO_3)_5](ClO_4)_2$ (**94**).

$$4[Ni(O_2CMe)\{(py)_2CO\}\{(py)_2C(OH)_2\}](ClO_4) + 3Ln(NO_3)_3{\cdot}6H_2O + 8EtOH \rightarrow [LnNi_2(H_2O)(NO_3)\{(py)_2C(OEt)O\}_4]_2[Ln(NO_3)_5](ClO_4)_2 + 4MeCO_2H + 2HClO_4 + 20H_2O \quad (5)$$

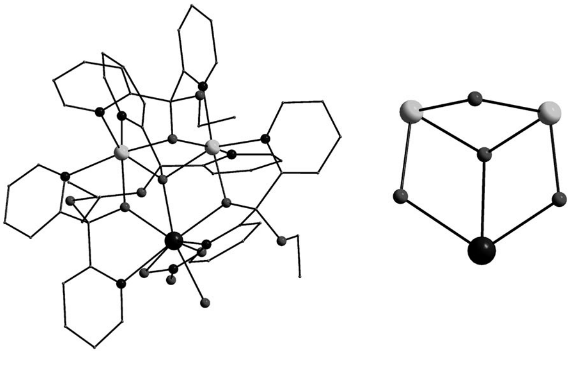


Figure 15. The molecular structure (left) and the $\{Ni_2Tb(\mu_2\text{-}OR'')_3(\mu_3\text{-}OR'')\}^{3+}$ core (right) of the $[Ni_2Tb(H_2O)(NO_3)\{(py)_2C(OEt)O\}_4]^{2+}$ cation that is present in complex **91**.

Surprisingly, the direct reactions of the appropriate simple Ni^{II} or Co^{II} and Ln^{III} salts in the presence of $(py)_2CO$ and $MeCO_2^-$ ions in EtOH give complexes containing very similar (but not identical) defective cubane, heterometallic trinuclear cations[113] and ClO_4^- ions as the only counteranions, according to the general balanced Equation (6). This fact emphasizes the dependence of the chemical and structural identity of the products on a number of synthetic and crystallization parameters. The molecular structure of the cation that is present in the representative complex $[GdNi_2(H_2O)(NO_3)\{(py)_2C(OEt)O\}_3\{(py)_2C(OH)O\}](ClO_4)_2$ (**95**) is shown in Figure 16. The $(py)_2C(OH)O^-$ ligand binds in the $3.3_{1,2}01_1 1_1$ (Scheme 12) mode, while the $(py)_2C(OEt)O^-$ ions act as 2.2011 (Scheme 9) and $2.2_{1,2}01_1 1_2$ (Scheme 12) ligands. The core in the members of this new family is $\{LnM_2(\mu_2\text{-}OR'')_3(\mu_3\text{-}OR''')\}^{3+}$ (M = Co, Ni). Complex **95** has a ground-state spin of 11/2, and the $Gd^{III}{\cdots}Ni^{II}$ exchange interaction is ferromagnetic.[113]

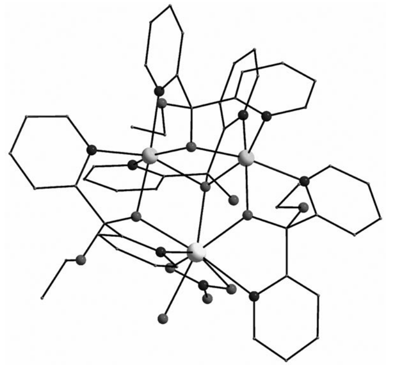


Figure 16. The molecular structure of the $[GdNi_2(H_2O)(NO_3)\{(py)_2C(OEt)O\}_3\{(py)_2C(OH)O\}]^{2+}$ cation that is present in complex **95**.

$$2M(ClO_4)_2{\cdot}6H_2O + Ln(NO_3)_3{\cdot}6H_2O + 4(py)_2CO + 4NaO_2CMe{\cdot}3H_2O + 3EtOH \rightarrow [LnM_2(H_2O)(NO_3)\{(py)_2C(OEt)O\}_3\{(py)_2C(OH)O\}](ClO_4)_2 + 4MeCO_2H + 2NaNO_3 + 2NaClO_4 + 28H_2O \quad (6)$$

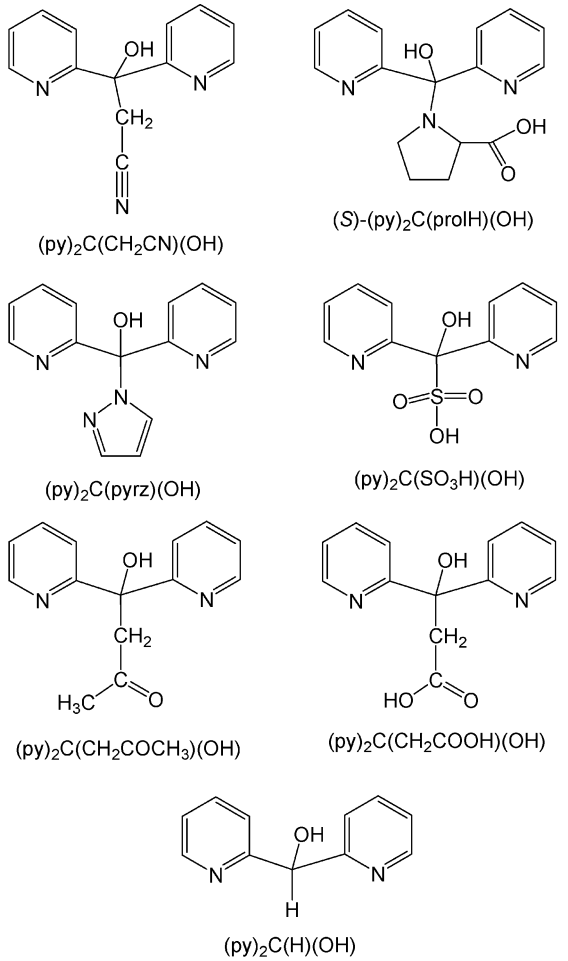
3.5. Unusual Reactivity Chemistry of Coordinated $(py)_2CO$

Recent studies have shown that attack by nucleophiles other than H_2O and alcohols (discussed until now) on the carbonyl C atom of $(py)_2CO$ *in the presence of divalent metals* generates the ligands shown in Scheme 13, which can be deprotonated to yield exciting organic chemistry of metal complexes and structurally interesting clusters. The molecules in Scheme 13, along with $dpkmeH_2$ already discussed (part 3.3, Scheme 11), can be considered as a *second generation* family of ligands derived from $(py)_2CO$.

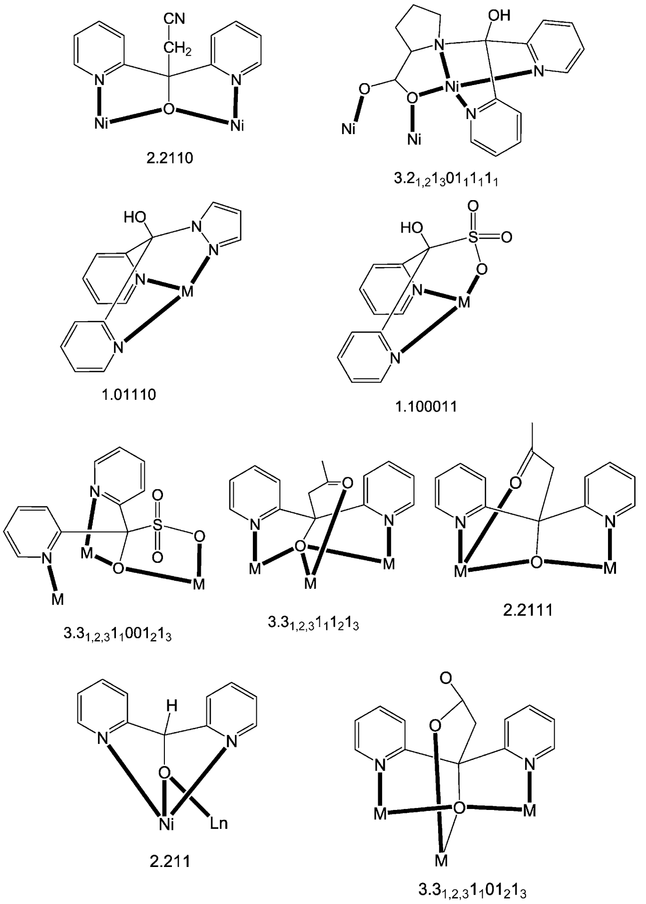
Reaction of $(py)_2CO$ with $Ni(O_2CMe)_2{\cdot}4H_2O$ and N_3^- in the presence of *t*BuOK as a catalytic base in MeCN generates compound $\{K_2(H_2O)_2\}\{K[Ni_6(6.222\text{-}CO_3)(2.200\text{-}N_3)_6(O_2CMe)_3\{(py)_2C(CH_2CN)O\}_3]\}_2$ (**96**), which is composed of two large $\{Ni_6(2.200\text{-}N_3)_6\}^{6+}$ circles joined by a $\{K_2(H_2O)_2\}^{2+}$ unit forming a new sandwich-type, high-spin K_4Ni_{12} cluster.[114] The ligand $(py)_2C(CH_2CN)O^-$ (Scheme 13) is generated in situ as a result of the cyanomethylation of the ketone; the anion behaves as a 2.2110 ligand (Scheme 14). It should be noted that cluster $[Ni_4(N_3)_2(O_2CMe)_2\{(py)_2C(OH)O\}_4]$ (**97**) is obtained if such a reaction is carried out in MeCN without *t*BuOK, which suggests that the presence of the strong base is the key to performing such a ligand reaction. This reaction to β-hydroxy nitriles may be potentially useful for the addition of nitrile anions to aldehydes or ketones, which would lead to an important group of synthetic organic intermediates.

Reactions of $M(O_2CMe)_2{\cdot}4H_2O$, $(py)_2CO$ and L-proline in CH_2Cl_2 (M = Co) or $EtOH/H_2O$ (M = Ni) under reflux gives the isomorphous chiral complexes with the formula $\{Na[M_4(O_2CMe)_3\{(py)_2C(prol)(OH)\}_3](ClO_4)_{1.5}(H_2O)_{1.5}\}(ClO_4)(OH)_{0.5}$ (M = Co, **98**; M = Ni, **99**).[115] The chiral intermediate (*S*)-$(py)_2C(prolH)(OH)$ (Scheme 13) can not be isolated. The two complexes present a rare flattened tetrahedral metal skeleton. The (*S*)-$(py)_2C(prol)(OH)^-$ ion binds in the $3.2_{1,2}1_3 01_1 1_1 1_1$ mode (see Scheme 14). Interestingly, the Co^{II}_4 cluster behaves as a ferromagnet. This is the first report of a tertiary carbinol derived from metal-assisted nucleophilic addition of a secondary amino acid to a ketone, which provides a new synthetic route to tertiary carbinol metal complexes, as well as insights into chiral secondary amino acid derivatives.

In very belated continuation of their earlier work with $(py)_2CO$,[116] Robson's group reported in 2006 unambiguous crystallographic evidence that, upon reaction with pyr-



Scheme 13. The second generation family of ligands derived from $(py)_2CO$. Note that none of them exist as free species but are found only in their respective metal complexes.



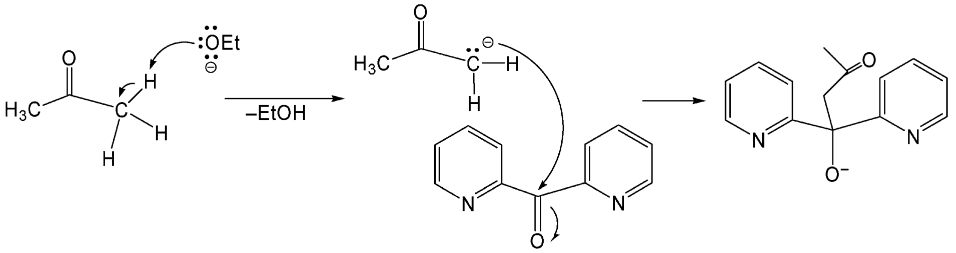
Scheme 14. The crystallographically established coordination modes of the second-generation ligands derived from $(py)_2CO$ and the Harris notations[3] that describe these modes.

azole in the presence of Ni^{2+}, a new C–N bond between the ketone C atom and a pyrazole (pyrzH) N atom is formed to generate a N_3 tridentate ligand, $(py)_2C(pyrz)(OH)$ (Scheme 13).[117] This chemistry is extremely simple: the reaction is conducted in aqueous solution at 20 °C. There is no evidence for any reaction whatsoever between pyrzH and $(py)_2CO$ in the absence of the metal ion, but when $Ni(NO_3)_2·6H_2O$ is present, single crystals of $[Ni\{(py)_2C(pyrz)(OH)\}_2](NO_3)$ (**100**) separate. The two 1.01110 neutral ligands (Scheme 14) chelate in a *facial* manner, the two pyrazole units being *trans* to one another.

Aqueous solutions containing $(py)_2CO$, various divalent transition-metal salts, and the bisulfate ion in 2:1:2 proportions afford, in a one-pot system, crystalline products containing electrically neutral complexes of composition *fac*-$[M\{(py)_2C(SO_3)(OH)\}_2]$, in which the tridentate chelating ligand is the monoanion of $(py)_2C(SO_3H)(OH)$ (see Scheme 13), generated by formation of a new C–S bond between the ketone C atom and the sulfite S atom. The M = Mn (**101**), Fe (**102**), Ni (**103**), Zn (**104**), and Cd (**105**) members of this family have been structurally characterized.[117] The monoanionic ligands adopt the 1.100011 mode.

Cubane-like, chiral complexes $[M_4\{(py)_2C(SO_3)(O)\}_4]$ (M = Mn, **106**; M = Zn, **107**) can be obtained in H_2O directly from $(py)_2CO$ in one-pot reaction systems, if a base as weak as $MeCO_2^-$ is present to deprotonate the OH group of the initial $(py)_2C(SO_3)(OH)^-$ addition compound.[117] The reactions are carried out at 120 °C in sealed tubes. The doubly deprotonated ligand binds in the $3.3_{1,2,3}1_{1}001_{2}1_{3}$ mode (Scheme 14), and its μ_3-O^- atom plays the role of forming the cubane. When excess Na_2SO_3 is used in similar one-pot reaction mixtures, the monoanionic complexes $Na[M_3Na\{(py)_2C(SO_3)(O)\}_4]$ (M = Mn, **108**; M = Co, **109**; M = Zn, **110**) with an $\{M_3Na(\mu_3\text{-}O)_4\}^{3+}$ core are formed;[117] three out of the four sulfonate residues associate with the Na^I center of the core.

Our group has recently contributed to the metal cluster chemistry of some of the ligands shown in Scheme 13. For example, the 1:1 reaction of $Ni(ClO_4)_2·6H_2O$ and $(py)_2CO$ in Me_2CO, in the presence of one equivalent of NaOEt, yields the cubane complex $[Ni_4\{(py)_2C(CH_2COCH_3)(O)\}_4](ClO_4)_4$ (**111**, Figure 17) through a Ni^{II}-assisted



Scheme 15. The proposed mixed-aldol-condensation mechanism that leads to the coordinated $(py)_2C(CH_2COCH_3)(O)^-$ ligand; the Ni^{II} ion stabilizes the enolate intermediate (not shown) and the ketone/alkoxido product.

mixed-aldol-condensation-type mechanism (Scheme 15),[118] as summarized in Equation (7). The monoanionic ligand binds in the $3.3_{1,2,3}1_11_21_3$ mode (see Scheme 14).

$$4Ni(ClO_4)_2\cdot 6H_2O + 4(py)_2CO + 4NaOEt + 4(CH_3)_2CO \rightarrow [Ni_4\{(py)_2C(CH_2COCH_3)(O)\}_4](ClO_4)_4 + 4NaClO_4 + 4EtOH + 24H_2O \quad (7)$$

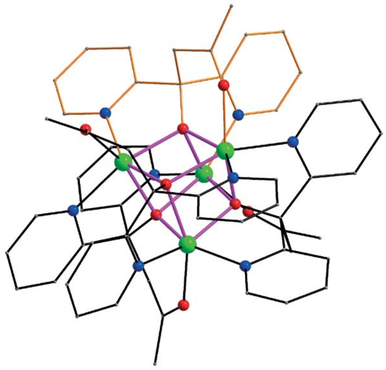


Figure 17. The molecular structure of the cation $[Ni_4\{(py)_2C(CH_2COCH_3)(O)\}_4]^{4+}$ that is present in complex **111**. Color code: Ni^{II} green, O red, N blue, C gray.

Repeating the reaction that gives complex **111** but simply changing the base from NaOEt to LiOH and the solvent from Me_2CO to Me_2CO/H_2O produces a completely different product: the pentanuclear cluster $[Ni_5\{(py)_2C(CH_2COCH_3)(O)\}\{(py)_2C(OH)O\}_4\{(py)_2CO_2\}](ClO_4)_3$ (**112**).[118] The core consists of a $\{Ni_4(\mu_3\text{-}OR'')_3(\mu_3\text{-}OR''')\}^{4+}$ cubane linked to an external Ni^{II} ion through the transformed, 2.2111 $(py)_2C(CH_2COCH_3)(O)^-$ (Scheme 14) derivative, one 2.2011 $(py)_2C(OH)O^-$ ion (Scheme 9), and the unique 4.3111 $(py)_2CO_2^{2-}$ ligand (Scheme 10).

The $Mn(ClO_4)_2\cdot 6H_2O/(py)_2CO/NaOEt$ (1:1:2) reaction system in Me_2CO/DMF gives the cubane cluster $[Mn^{II}_4\{(py)_2C(CH_2COO)(O)\}_4]$ (**113**)[118] by a metal-ion-promoted oxidative cleavage of the ketone C–C bond in the $(py)_2C(CH_2COCH_3)(O)^-$ ligand [see Equation (8)]. The dianionic $(py)_2C(CH_2COO)(O)^{2-}$ carboxylate/alkoxido ligand adopts the $3.3_{1,2,3}1_101_21_3$ coordination mode (Scheme 14). Note that this ligand is somewhat related to the hemiketal derivative dpkme^{2-} (Scheme 11) that exists in complex **68** (Figure 12).[99]

$$4Mn(ClO_4)_2\cdot 6H_2O + 4(py)_2CO + 8NaOEt + 4CH_3COCH_3 \rightarrow [Mn_4\{(py)_2C(CH_2CO_2)(O)\}_4] + 4CH_4 + 8NaClO_4 + 8EtOH + 20H_2O \quad (8)$$

We have recently prepared[118] a family of mixed 3d/4f metal "stars" of the general formula $[LnNi_3\{(py)_2C(H)(O)\}_6](ClO_4)_3$ in EtOH under solvothermal conditions, e.g. Ln = Gd (**114**), Tb (**115**), Dy (**116**), etc. The monoanion of the hitherto unknown molecule $(py)_2C(H)(OH)$ (see Scheme 13) is produced in situ by the reduction of $(py)_2CO$. The formation of these complexes is summarized in Equation (9). The molecular structure of the cation of **114** is shown in Figure 18. The anion $(py)_2C(H)(O)^-$ behaves as a 2.211 ligand (Scheme 14). Preliminary results show that complex **115** behaves as a SMM.[118]

$$3Ni(ClO_4)_2\cdot 6H_2O + Ln(NO_3)_3\cdot 6H_2O + 6(py)_2CO + 6CH_3CH_2OH + 6NaO_2CMe\cdot 3H_2O \rightarrow [LnNi_3\{(py)_2C(H)O\}_6](ClO_4)_3 + 6CH_3CHO + 6MeCO_2H + 3NaClO_4 + 3NaNO_3 + 42H_2O \quad (9)$$

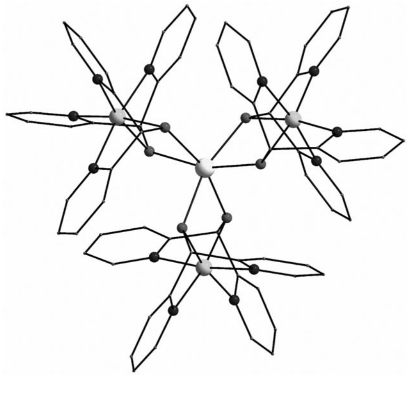
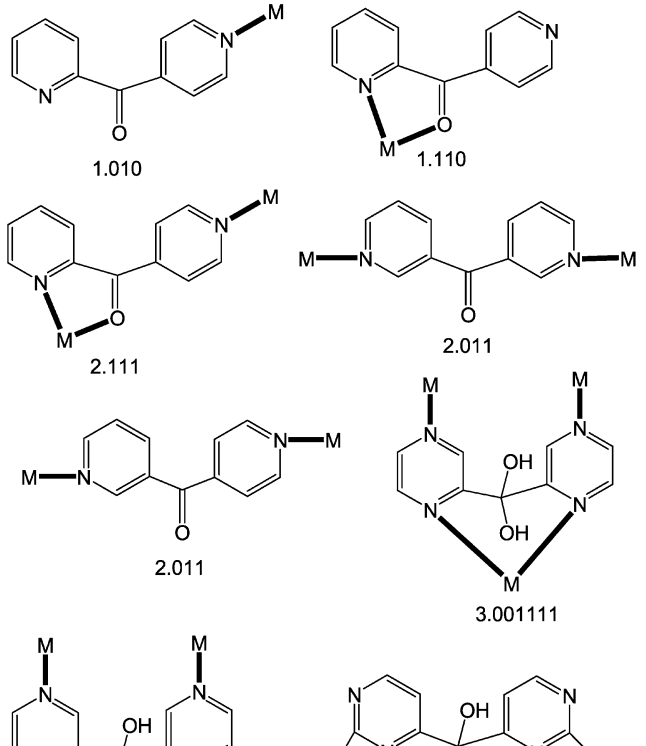


Figure 18. The molecular structure of the cation $[GdNi_3\{(py)_2C(H)O\}_6]^{3+}$ that is present in complex **114**.

It should be mentioned at this point that to date most cluster synthesis has involved "conventional" coordination techniques, i.e., solution chemistry under atmospheric pressure and at temperatures limited to the boiling points of the solvents.[45] However, the application of higher temperatures and pressures is likely to lead to the isolation of different products and is therefore an alternative synthetic strategy that should not be ignored. Solvothermal techniques[119] allow the application of high temperatures to reactions in low-boiling solvents and represent an excellent method for the preparation of pure, crystalline clusters in high yields.

4. Metal Complexes of Other Dipyridyl Ketones, Di-2-pyrazinyl Ketone, and Di-2-(4-methylthio)-pyrimidyl Ketone

The ligands that are discussed in this section are shown in Scheme 3. Metal complexes of (py)CO(4′-py), (3-py)$_2$CO, (pyz)$_2$CO, and (Spym)$_2$CO [di-2-(4-methylthio)pyrimidyl ketone] are limited in number. The reason is simple: they are not available on the market and their synthesis is difficult. The crystallographically established coordination modes of the ligands are shown in Scheme 16. This area is dominated by research from Mak's group.



Scheme 16. The coordination modes of other dipyridyl ketones [(py)CO(4′-py) and (3-py)$_2$CO], (pyz)$_2$CO, and (Spym)$_2$CO with the Harris notations[3] that describe these modes.

The reactions of 2-pyridyl-4′-pyridyl ketone (or 2-pyridinyl-4′-pyridinylmethanone), (py)CO(4′-py), prepared by the reaction of methyl isonicotinate and 2-lithiopyridine (generated in situ from 2-bromopyridine and *n*BuLi), with Zn^{II}, Co^{II}, and Cd^{II} sources give rise to the 1D coordination polymers $\{[Zn(H_2O)_3\{(py)CO(4'\text{-}py)\}](NO_3)_2\}_n$ (**117**), $\{[Co(H_2O)_2\{(py)CO(4'\text{-}py)\}_2](ClO_4)_2\cdot 2H_2O\}_n$ (**118**), and $\{[Cd_2(H_2O)_4\{(py)CO(4'\text{-}py)\}_4](ClO_4)_4\cdot 3H_2O\}_n$ (**119**).[120] The polymeric chains of each compound are linked into 3D networks by intermolecular H-bonding, with additional π–π stacking interactions in the case of the Co^{II} and Cd^{II} complexes. The molecule (py)CO(4′-py) exhibits different ligation modes in the 1D polymers, acting as a monodentate (1.010), bidentate chelating (1.110), or tridentate chelating-bridging (2.111) ligand.[120]

Di-3-pyridyl ketone, (3-py)$_2$CO, is synthesized by the reaction between 3-lithiopyridine and methyl nicotinate in anhydrous Et$_2$O at –78 °C under N$_2$.[121a] A series of Ag^I complexes with the general formula $\{[Ag\{(3\text{-}py)_2CO\}](X)\}_n$ (X = BF$_4$, **120**; X = ClO$_4$, **121**; X = NO$_3$, **122**; X = CF$_3$SO$_3$, **123**; X = PF$_6$, **124**) have been prepared.[121a] Argentophilic interactions, π–π stacking, Ag···X interactions, and C–H···X (X = O, F) and C–H···O=C H-bonding contribute to different extents in the construction of helical (**120**–**122**) or zigzag (**123**, **124**) chains, with the ligand in the *N,N′*-bridging mode (2.011) in all cases. 1:2 M^{II}/(3-py)$_2$CO (M = Cu, Cd) compounds have also been reported.[121b] The complexes exhibit 1D and 2D architectures according to the extent to which the ClO$_4^-$ and BF$_4^-$ counteranions interact with the metal center; the ligand binds in the 2.011 mode.

In an effort to synthesize new mixed metal oxide phases, Montney and LaDuca have very recently reported initial studies[122] on the Cu^{II}/Mo^{VI} coordination chemistry of 3-pyridyl-4′-pyridyl ketone, (3-py)CO(4′-py), prepared by the reaction of 3-lithiopyridine with methyl isonicotinate in a manner similar to that reported by Mak for the synthesis of (3-py)$_2$CO.[121a] Hydrothermal treatment of CuCl$_2$·2H$_2$O, MoO$_3$ and (3-py)CO(4′-py) in a 1:1:2 molar ratio affords the new mixed metal oxide phases $[Cu^{II}_2(MoO_4)_2(H_2O)\{(3\text{-}py)CO(4'\text{-}py)\}]_n$ (**125**) or $[Cu^I_4(Mo_8O_{26})\{(3\text{-}py)CO(4'\text{-}py)\}_4]$ (**126**), depending on the pH of the initial reaction mixture.[122] Compound **125** is a 2D polymer, while **126** manifests an unprecedented "X-rail" 1D structure with $(6^28)_4(6^6)$ topology. The molecule (3-py)CO(4′-py) acts as a 2.011 ligand in both compounds. The variable-temperature magnetic susceptibility behavior of **125** was fitted to a linear tetramer model with both ferro- and antiferromagnetic exchange interactions.

The ligand di-2-pyrazinylmethanone, (pyz)$_2$CO, can be synthesized by the reaction of 2-lithiopyrazine and methyl-2-pyrazine carbonate in anhydrous Et$_2$O at –70 °C.[123] Two Ag^I coordination polymers of its *gem*-diol (pyz)$_2$C(OH)$_2$, namely $\{[Ag\{(pyz)_2C(OH)_2\}](CF_3SO_3)\}_n$ (**127**) and $\{[Ag\{(pyz)_2C(OH)_2\}](CF_3CO_2)\}_n$ (**128**), have been characterized by X-ray crystallography.[123] The diol behaves as a 3.001111 and 4.101111 ligand in **127** and **128**, respectively. A (4,4) net is found in **127**. In the case of **128**, the Ag^I ion functions as a rare 5-connected node to conjunct the (pyz)$_2$C(OH)$_2$ ligands into an extended network that can be viewed as an α-Po topology of the NaCl type. Alternatively, this network can be rationalized as a 4-connected net having the Schläfli symbol 4^368^2, which is related to the Gismondine topology,[124] by treating the Ag^I center and the whole ligand as separate nodes (Figure 19).

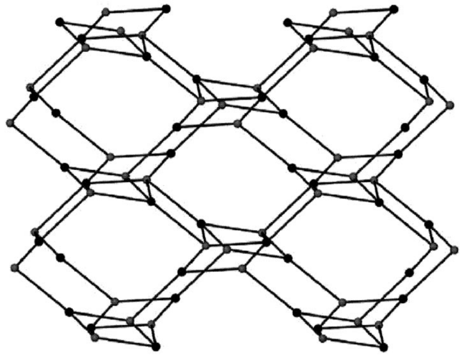
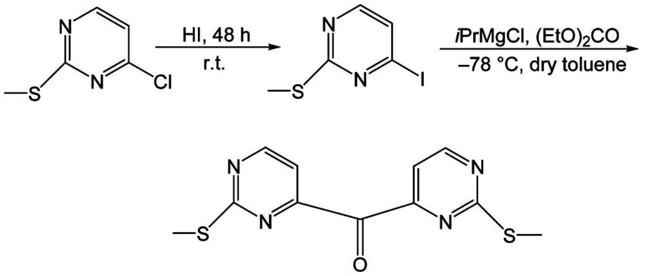


Figure 19. Topological structure of $\{[Ag\{(pyz)_2C(OH)_2\}](CF_3CO_2)\}_n$ (**128**). The gray and black balls represent the Ag^I ion and the diol ligand, respectively, which are considered as separate nodes in the Schläfli symbol $4^3 68^2$. The figure is reproduced from ref.[123] by permission.

The interesting ligand di-2-(4-methylthio)pyrimidyl ketone, $(Spym)_2CO$, was synthesized[125] in a two-step reaction from commercially available 4-chloro-2-methylthiopyrimidine (see Scheme 17).



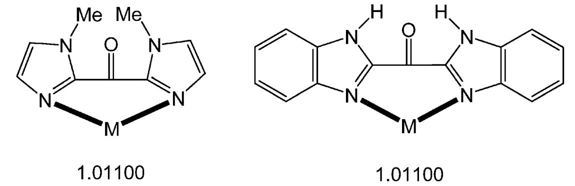
Scheme 17. The two-step synthesis of $(Spym)_2CO$.

The synthesis, crystal structure, and magnetic properties of the hexametallic Fe^{III} cluster $[Fe_6O_2(O_2CCMe_3)_{10}(OH)_2\{(Spym)_2C(OH)O\}_2]$ (**129**) have been recently reported by the group of McInnes and Winpenny.[125] Compound **129** consists of a planar array of six Fe^{III} ions comprising two $\{Fe_3(\mu_3\text{-}O)\}^{7+}$ subunits that are linked at two of their apices, each through one μ_2-hydroxido and two μ_2-carboxylato groups. The anion $(Spym)_2C(OH)O^-$ behaves as a 2.20001000 ligand. Although **129** has a well-isolated $S = 5$ ground state with a negative magnetic anisotropy (as proven by variable-temperature W-band EPR studies), it is not a SMM bcause of its large rhombicity.

2-Pyridyl *N*-methyl-2-imidazolyl ketone, (py)CO(Meim), reacts with $Au^{III}(Me)_2NO_3$, $CuSO_4{\cdot}5H_2O$, and $Ni(NO_3)_2{\cdot}6H_2O$ to form complexes that do not involve hydration of the ligand;[53h] the products have not been characterized crystallographically.

5. Developments in the Coordination Chemistry of Other X–CO–X Ligands

A ligand closely related to $(py)_2CO$, bis(*N*-methyl-2-imidazolyl) ketone, [$(Meim)_2CO$, Scheme 3], reacts with $CuSO_4{\cdot}5H_2O$ in H_2O to form complex $[Cu(H_2O)_2\{(Meim)_2CO\}(SO_4)]$ (**130**).[53h] The complex has square-pyramidal coordination for Cu^{II}; the *N,N′*-chelating (1.01100) ligand (Scheme 18) is in the basal plane with a H_2O molecule and monodentate SO_4^{2-} ion, and a H_2O molecule is coordinated axially. The same coordination mode is observed for the ligand in the square-pyramidal complex $[Cu\{(Meim)_2CO\}(NTAH)]$ (**131**), where $NTAH^{2-}$ is the dianion of nitrilotriacetic acid.[126]



Scheme 18. The crystallographically established coordination modes of $(Meim)_2CO$ and $(bnzim)_2CO$ with the Harris notations[3] that describe these modes.

An impressive Co^{II}-ion catalyzed ketonization of the methylene group of bis(benzimidazol-2-yl)methane [$(bnzim)_2CH_2$] by O_2 has been reported by Yao's group.[127] The mononuclear, distorted tetrahedral complex $[Co\{(bnzim)_2CO\}Cl_2]$ (**132**), where $(bnzim)_2CO$ is bis(benzimidazol-2-yl)methanone (Scheme 3), is obtained by the reaction of $CoCl_2{\cdot}6H_2O$ and $(bnzim)_2CH_2$ in MeCN/MeOH. The ketone ligand binds in the 1.01100 mode (see Scheme 18). The ketonization mechanism, followed by UV/Vis spectroscopic and electrochemical techniques, involves an intermediate superoxidocobalt(III) species and a Co^{II} complex bearing the $(bnzim)_2C(H)(OH)$ ligand.[127]

In an attempt to prepare novel coordination polymers, the group of Boudalis – in collaboration with our group – have recently studied the coordination chemistry of 1,1′-carbonyldiimidazole [$(im)_2CO$ (Scheme 3)], a well-known reagent in organic synthesis.[128] The free ligand exhibits very high reactivity towards nucleophilic reagents, because of the electron attraction exerted from both sides on the carbonyl group by the heterocycle. Thus, H_2O hydrolyzes $(im)_2CO$ at room temperature within seconds, with vigorous evolution of CO_2 as shown in Equation (10).[129] The free ligand also reacts with alcohols, forming diesters of carbonic acid or imidazole-*N*-carboxylic esters and yielding free imidazole.[129] Therefore, at the outset of our efforts we were aware that $(im)_2CO$ could not be incorporated in metal complexes in aqueous or alcoholic reaction media. However, we hoped that such reactions would likely yield coordination polymers containing the bridging imidazolato(–1) ligand (im^-), different from those obtained with the use of imH as starting material. This has, indeed, turned out to be the case.

$$(im)_2CO + H_2O \rightarrow 2imH + CO_2\uparrow \qquad (10)$$

The $[Cu_2(H_2O)_2(O_2CMe)_4]/(im)_2CO$ reaction system in EtOH yields the new polymeric species, $[Cu(EtOH)(im)(imH)(O_2CMe)]_n$ (**133**),[130] and the known[131] compound $[Cu(im)_2]_n$ (**134**). The two complexes can be prepared independently in pure form. In Equations (11), (12), and (13) we propose a simplistic reaction scheme that may explain the observed $(im)_2CO$-to-im^- transformation. It is difficult to decide whether the step represented by Equation (11) is Cu^{II}-assisted. The metal center may polarize the carbonyl group by coordination of the O atom, and EtOH can attack the carbonyl C atom to generate the tetrahedral intermediate before the formation of the ester. It is noteworthy that a similar transformation of $(im)_2CO$ to im^-, leading to compound $[Cu_3(ClO_4)_4(Him)_8(im)_2]_n$ (**135**), has been reported by Ghosh and co-workers.[132] However, this complex can be prepared by using imH as starting material.[133]

$$\mathrm{EtOH + im{-}CO{-}im \rightarrow Et{-}O{-}CO{-}im + imH} \tag{11}$$

$$\mathrm{Et{-}O{-}CO{-}im + H_2O \rightarrow EtOH + imH + CO_2\uparrow} \tag{12}$$

$$\mathrm{imH + MeCO_2^-} \overset{Cu^{2+}}{\rightleftharpoons} \mathrm{im^- + MeCO_2H} \tag{13}$$

Complex **133** comprises neutral zigzag chains (Figure 20), in which the 2.11 im^- ligand bridges two neighboring Cu^{II} ions. Each square-pyramidal metal center is coordinated to two imidazolato N atoms, the pyridine-type N atom of the terminal neutral imidazole ligand (imH), one $MeCO_2^-$ O atom, and the EtOH O atom. The dc magnetic susceptibility data for **133** have been analyzed according to the Bonner–Fisher model for an equally spaced $S = 1/2$ chain, revealing antiferromagnetic $Cu^{II}\cdots Cu^{II}$ exchange interactions ($J = -33.5\ cm^{-1}$ using the $H = -2J\Sigma\hat{S}_i\hat{S}_{i+1}$ spin Hamiltonian).

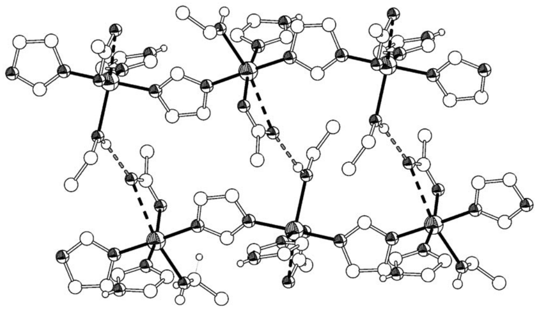
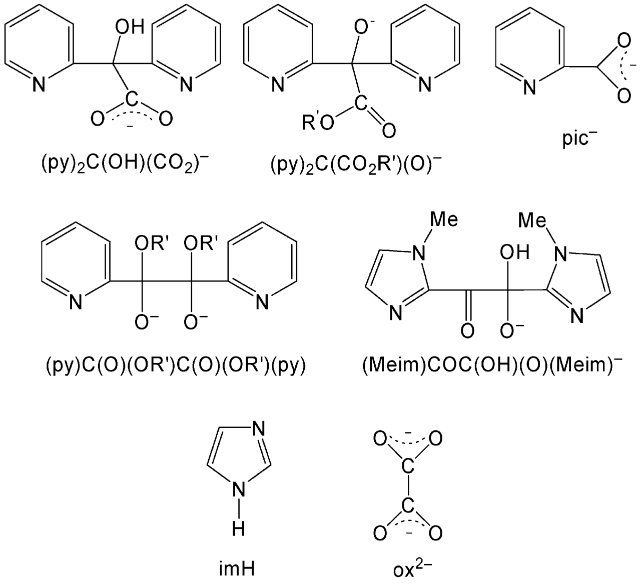


Figure 20. A H-bonded pair of portions of the 1D chains in $[Cu(EtOH)(im)(imH)(O_2CMe)]_n$ (**133**). Weak Cu–O(acetato) interactions are shown as solid dashed lines and H bonds are shown as hollow dashed lines.

The $Cu(NO_3)_2\cdot 3H_2O/(im)_2CO$ in EtOH[130] leads to the preparation of the known complex *trans*-$[Cu(imH)_4(NO_3)_2]$ (**136**).[131b] With terephthalate(–2) (tp^{2-}) instead of $MeCO_2^-$, the product is the new, 1D, linear coordination polymer $[Cu(H_2O)(imH)_2(tp)]_n$ (**137**).[130] Adjacent square-pyramidal Cu^{II} ions are singly bridged by the bis(monodentate) tp^{2-} ligand, while two monodentate imH groups and one H_2O molecule complete 5-coordination at each metal center. It is important to note that polymers **133** and **137** can not be prepared from conventional reactions that employ imH and the respective carboxylate as starting materials. This demonstrates the usefulness of $(im)_2CO$ in the preparation of interesting coordination polymers that can not be obtained by the use of Him.

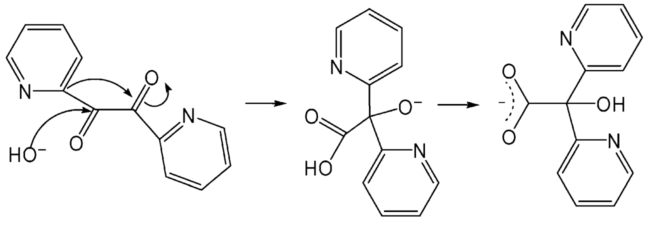
6. The X–CO–CO–X Family of Ligands: An Unexplored Area in Coordination Chemistry and Useful Reagents for Inorganic Synthesis

The intermediate ligands discussed in this section are shown in Scheme 19. The ligand representative of this family is 2,2′-pyridil (1,2-di-2-pyridylethanedione), (py)CO-CO(py) (Scheme 3); its crystal structure is known.[134] This ligand undergoes[135] a transition-metal-ion-promoted benzilic acid rearrangement.[135] The first step of the reaction involves nucleophilic attack of base on an *O*-bonded carbonyl group to form a hydrate, followed by the migration of the 2-pyridyl group from the C atom attacked by OH^- to the adjacent C atom; thus, the carbon center initially under attack becomes a carboxylate (Scheme 20). In this case, the benzilic acid rearrangement products can be isolated as metal complexes.[48] For example, the product of the benzilic-acid-type rearrangement in the case of (py)CO-CO(py), the 2,2′-pyridilate(–1) ion $[(py)_2C(OH)(CO_2)^-$, (Scheme 19)], was isolated as the crystalline *trans*-$[Ni\{(py)_2C(OH)(CO_2)\}_2]$ (**138**);[136] the ligand binds in the 1.10011 mode (Scheme 21).

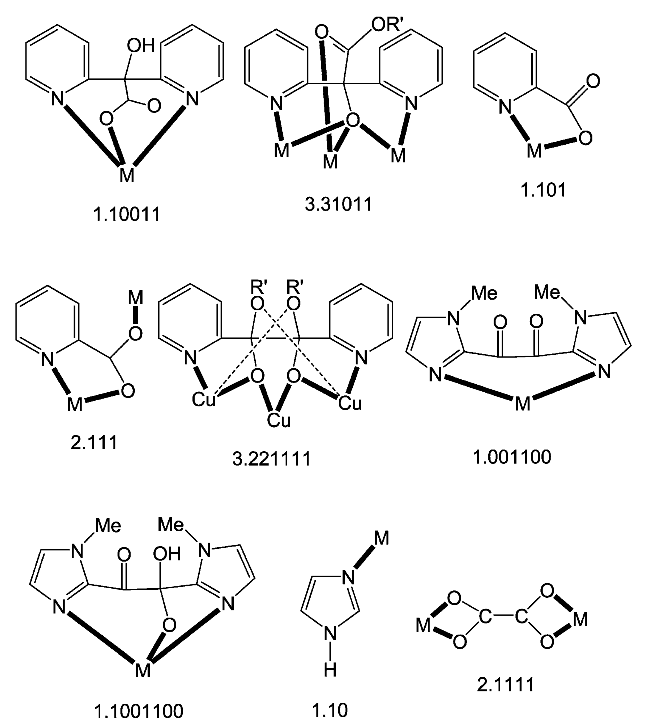


Scheme 19. The intermediate and final ligands discussed in Section 6 of this Microreview.

Robson and co-workers have isolated complexes in which the carboxylic group of 2,2′-pyridilate has undergone esterification;[117] the ester group is also able to act as a donor to the metal ion. Reaction of (py)COCO(py) and $Ca(NO_3)_2\cdot 4H_2O$ in basic alcohol solution at 90 °C in a sealed tube, which proceeds by a similar benzilic-acid-type rearrangement, gives cubane compounds $[Ca_4(NO_3)_4\{(py)_2C(CO_2R')(O)\}_4]$ (R′ = Me, **139**; R′ = Et, **140**). The Ca^{II} centers are equivalent and eight-coordinate. The metal coordi-



Scheme 20. The M^{II}-promoted conversion of 2,2′-pyridil to 2,2′-pyridilate(–1).[117] This sketch is intended to indicate the skeletal rearrangement within the organic fragment; no doubt the intermediates are coordinated to M^{II}.



Scheme 21. The crystallographically established coordination modes of the intermediate and final ligands discussed in Section 6 of this Microreview with the Harris notations[3] that describe these modes.

nation environment consists of three cubane-forming μ_3-alkoxido O atoms from three 3.31011 $(py)_2C(CO_2R')O^-$ ligands, two pyridyl donors from two separate ligands, an ester carbonyl O donor from a third ligand, and a chelating nitrato group.

The reactions of $MnCl_2{\cdot}4H_2O$ and $CuCl_2{\cdot}2H_2O$ with one equivalent of (py)COCO(py) in H_2O/MeOH yield complexes $[Mn(H_2O)_2(pic)_2]$ (**141**)[137] and $\{[Cu(pic)_2]{\cdot}2H_2O\}_n$ (**142**),[137,138] respectively, where pic^- is the picolinato ligand (Scheme 19); the pic^- ligand is a degradation product of (py)COCO(py). Complex **141** is mononuclear with the pairs of aqua ligands, carboxylate O donors, and 2-pyridyl N donors in *cis*, *cis*, and *trans* positions, respectively; the pic^- ion behaves as a 1.101 ligand (Scheme 21). In the 1D complex **142**, the pic^- ion serves as a 2.111 ligand (Scheme 21); there are weak antiferromagnetic exchange interactions between the Cu^{II} centers.[137] The Cu^{II} complex is also obtained by using $Cu(ClO_4)_2{\cdot}6H_2O$ as starting material.[139]

The use of (py)COCO(py) in reactions with Cu^{II} carboxylates in alcohols (R′OH; R′ = Et, *n*Pr) has led to structurally interesting clusters with the general formula $[Cu_5(OH)_2(O_2CR)_4\{(py)C(O)(OR')C(O)(OR')(py)\}_2(R'OH)_2]$ (R = Me, R′ = Et, **143**; R = Me, R′ = *n*Pr, **144**; R = Ph, R′ = Et, **145**).[140] The Cu^{II}-mediated alcoholysis of (py)COCO(py) to give the dianions (Scheme 19) of the bis(hemiketal)s (py)C(OH)(OR′)C(OH)(OR′)(py) involves a nucleophilic attack of R′OH molecules on the carbonyl groups.[140] The preparation of the representative complex **143** is summarized in Equation (14). The nature of the alcohol affects the identity of the product; reactions in MeOH lead to copper(II) picolinato complexes.[137–139,141] The temperature is also a particularly important synthetic parameter. If the reaction mixtures in EtOH or *n*PrOH are heated or refluxed, they yield exclusively copper(II) picolinato complexes.

$$5[Cu_2(O_2CMe)_4(H_2O)_2] + 4(py)COCO(py) + 12EtOH \rightarrow 2[Cu_5(EtOH)_2(OH)_2(O_2CMe)_4\{(py)C(O)(OEt)C(O)(OEt)(py)\}_2] + 12MeCO_2H + 6H_2O \qquad (14)$$

The molecular structures of the $Cu^{II}{}_5$ complexes are similar. The structure of **143** is shown in Figure 21. The planar pentanuclear assembly is composed of a rectangular arrangement of four Cu^{II} ions centered around the fifth. The Cu^{II} ions at each short edge of the rectangle are bridged by a hydroxido ligand, which also interacts weakly with the central metal. The $(py)C(O)(OR')C(O)(OR')(py)^{2-}$ ions behave as 3.221111 ligands (Scheme 21); the long (2.582–2.939 Å) Cu^{II}–OR′ distances suggest weak interactions. Terminal R′OH molecules and RCO_2^- groups (both monodentate and chelating) complete the coordination spheres of the peripheral Cu^{II} ions. Compounds **143**–**145** are the only structurally characterized complexes to date of any metal containing the anions $(py)C(O)(OR')C(O)(OR')(py)^{2-}$ as ligands.

Variable-temperature magnetic susceptibility studies reveal that the ground state of the complexes ($m_s = \pm 3/2$) has the central spin up and the four others down, or vice versa. Although the three J values are negative, the ground state does not correspond to an $m_s = 1/2$ value because of spin frustration, as one would expect from the geometry of the molecules.[140] The powder EPR spectrum of **143** displays a line at $g \approx 4.3$, characteristic of an effective $S = 3/2$ ground state.

Metal complexes of 3,3′- and 4,4′-pyridil are not known. Rogachev and co-workers calculated equilibrium geometry configurations for 2,2′-, 3,3′- and 4,4′-pyridil by using DFT methods (B3LYP/6-311G++**).[142] The *ortho*-position of N atoms in 2,2′-pyridil leads to significant changes in the electronic and energetic properties in comparison with the other two isomers. Thus, 2,2′-pyridil is less stable and has significant differences in charge distribution in comparison with the other two isomers, which can be explained by additional interactions between the 2-pyridyl N atoms and the O atoms from the neighboring carbonyl groups.

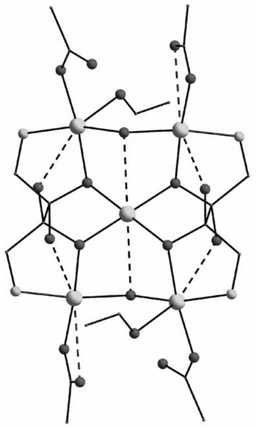


Figure 21. The molecular structure of [$Cu_5(EtOH)_2(OH)_2(O_2CMe)_4$-{(py)C(O)(OEt)C(O)(OEt)(py)}$_2$] (**143**). For clarity, all C atoms of the OEt groups of the organic ligand and most aromatic C atoms have been omitted. The dashed lines indicate weak interactions.

The frequent occurrence of two histidine binding sites for metal centers in proteins has prompted the development of many bis(imidazole)-containing chelating ligands for purposes of active-site modeling.[143] Among these ligands, bis(1-methylimidazol-2-yl)glyoxal [(Meim)COCO(Meim), Scheme 3] has been employed in connection with several metal ions.[143] A computational study of (Meim)COCO(Meim) as a free "molecule" (neutral, one-electron reduced and oxidized forms) and as a ligand with different coordination modes in complexes has also been reported.[144] Complexes *cis*-[MCl_2{(Meim)COCO(Meim)}] (M = Pd, **146**; M = Pt, **147**) were prepared and characterized through electrochemistry, spectroscopy, and for **147**, by X-ray structural analysis[143a] (see Figure 22). The seven-membered chelating ring formed through *N*,*N*′- or 1.001100 (Scheme 21) coordination of the ligand shows a boat conformation in agreement with DFT calculation results. Both the Pd^{II} and Pt^{II} complexes undergo reversible one-electron reduction in CH_2Cl_2. EPR, UV/Vis, and IR spectroelectrochemical techniques were employed to study the monoanions. The anionic radical complex *cis*-[$PtCl_2${(Meim)COCO(Meim)}]$^{\cdot-}$ exhibits a well-resolved EPR spectrum with small (but well-detectable) *g* anisotropy and an isotropic ^{195}Pt hyperfine coupling of 12.2 G. DFT calculations confirm the spin concentration in the *o*-semidione part of the radical complex with small delocalization to the bis(imidazolyl)metal component. The results show that EPR- and electroactive moieties can be linked to the *cis*-dichloroplatinum(II) group by imidazole coordination.

The boat-shaped, seven-membered chelating ring of the ligands has also been observed in the structurally characterized mononuclear complexes *fac*-[$Re^ICl(CO)_3${(Meim)-COCO(Meim)}] (**148**)[143b] and [$Rh^{III}Cl(C_5Me_5)${(Meim)-COCO(Meim)}] (**149**).[143c] The Ir^{III} analogue **150** reacts with H_2O to form complex [$Ir^{III}(C_5Me_5)${(Meim)-COC(OH)(O)(Meim)}](PF_6) (**151**)[143c] with the simultaneous elimination of HCl; the monoanion of the mono *gem*-diol form of the ligand binds in the 1.1001100 mode, Scheme 21, forming one five- and one six-membered chelating ring involving the alcoholate O atom. The complex dimerizes in the crystal through H bonding.

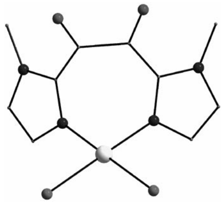


Figure 22. Molecular structure of *cis*-[$PtCl_2${(Meim)COCO-(Meim)}] (**147**) in the crystal.

The group of Boudalis, in collaboration with our group, has recently initiated a project aiming at the use of 1,1′-oxalyldiimidazole [(im)COCO(im), Scheme 3] for inorganic synthesis.[145] This ligand presents a structural similarity to (py)COCO(py) but contains *N*-imidazolyl instead of 2-pyridyl groups. Our goal is to see how incorporation of the former groups might affect the chemical and structural identity of the products. 1,1′-oxalyldiimidazole is a known reagent in organic[146] and analytical[147] chemistry. As in the case of $(im)_2CO$,[130] at the outset of our efforts we were aware that the ligand might exhibit metal-ion-assisted reactivity towards nucleophiles, because of the electron attraction exerted on each carbonyl group by the neighboring heterocycle. Thus, we expected that (im)COCO(im) would not remain intact during its incorporation into metal complexes in aqueous or alcoholic reaction media. However, we hoped that such reactions would likely give cluster or polymeric metal complexes containing decomposition "fragments" of (im)COCO(im), different from those obtained with the use of the simpler "fragments" as starting ligands. The [$Cu_2(H_2O)_2(O_2CMe)_4$]/(im)COCO(im) reaction system in 96% EtOH yields the new 1D coordination polymer [$Cu(imH)_2(ox)$]$_n$ (**152**),[145] where imH is the neutral imidazole and ox^{2-} is the oxalato(–2) ligand (Scheme 19). In Equations (15) and (16), we propose a simplistic reaction scheme that may explain the observed decomposition of the starting ligand to imH and ox^{2-}. Overall, the formation of **152** can be represented by Equation (17).

$$\text{(im)COCO(im)} + 2H_2O \xrightarrow{Cu^{2+}} 2\text{imH} + \text{HOOC–COOH} \tag{15}$$

$$\text{HOOC–COOH} + 2MeCO_2^- \rightarrow {}^-\text{OOC–COO}^- + 2MeCO_2H \tag{16}$$

$$n[Cu_2(H_2O)_2(O_2CMe)_4] + 2n\text{(im)COCO(im)} + 2nH_2O \rightarrow 2[Cu(imH)_2(OOC–COO)]_n + 4nMeCO_2H \tag{17}$$

With the identity of **152** having been established by single-crystal X-ray crystallography (Figure 23), a convenient synthesis of the pure material by using simpler ligands was sought. Various [$Cu_2(H_2O)_2(O_2CMe)_4$]/imH/oxH_2 reaction schemes in EtOH yielded repeatedly the known complex [$Cu(imH)_2(ox)$]$_2$[$Cu(H_2O)(imH)_2(ox)$]$_2$ (**153**), consisting of the dinuclear [$Cu(imH)_2(ox)$]$_2$ unit and a pair of H-bonded, mononuclear $[Cu(H_2O)(imH)_2(ox)]$ moieties.[148] Thus, the employment of (im)COCO(im) remains the only method to date for the preparation of **152**.

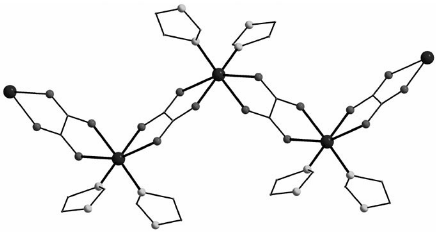
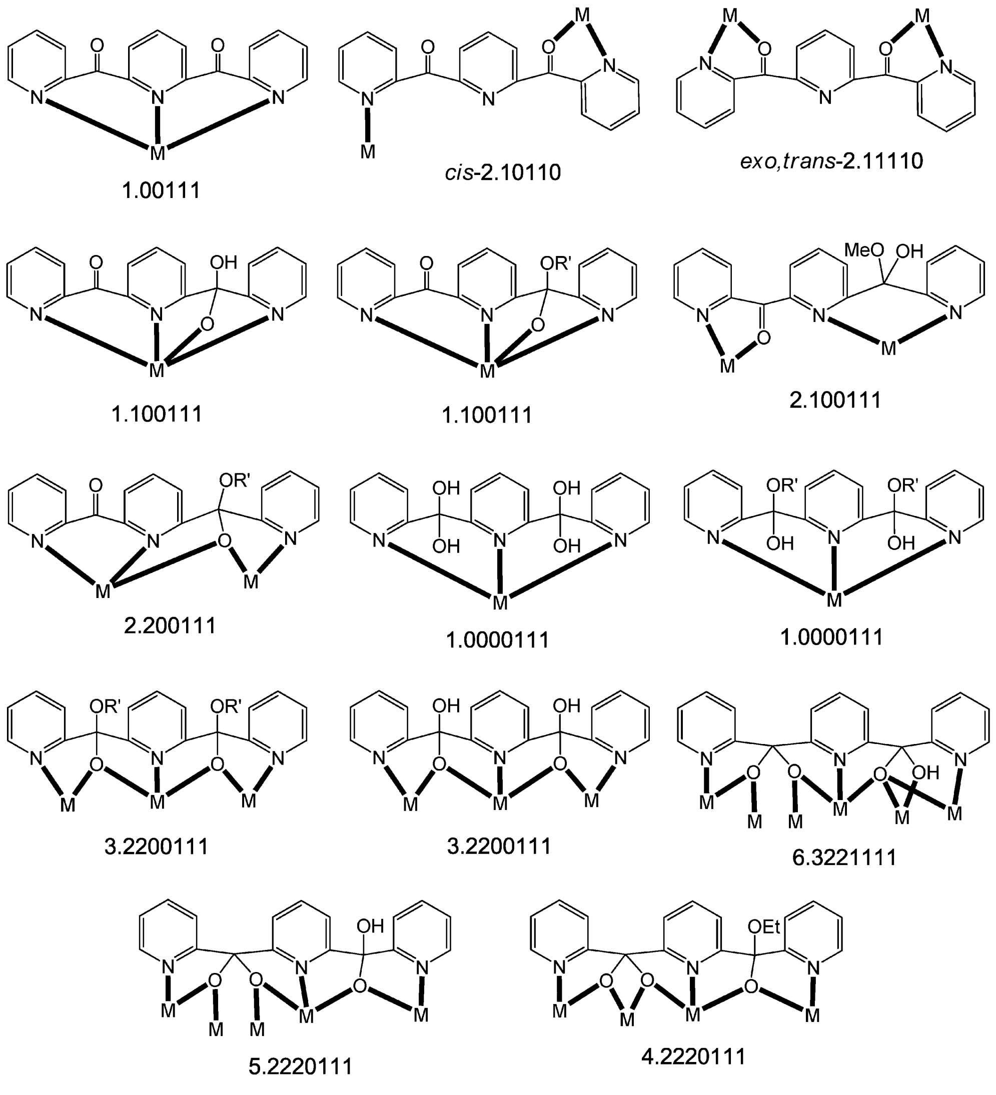


Figure 23. A portion of the zigzag chain present in complex **152**.

Complex **152** comprises neutral, zigzag chains in which the 2.1111 ox^{2-} ligand (Scheme 21) bridges two neighboring Cu^{II} centers; two *cis* 1.10 imH groups (Scheme 21) complete a Jahn–Teller-distorted octahedral geometry at the metal. The variable-temperature dc magnetic susceptibility data for the complex reveal antiferromagnetic $Cu^{II}\cdots Cu^{II}$ exchange interactions.[145]

7. The Impressive Coordination Chemistry of Di-2,6-(2-pyridyl)pyridine

The ligand di-2,6-(2-pyridyl)pyridine or 2,6-pyridinediylbis(2-pyridyl)methanone, (py)CO(py)CO(py) (Scheme 3), can be considered as an expansion of $(py)_2CO$. Although it had been synthesized in the late 1990s,[149] its ligand properties remained unexplored until 2005. The ligand can potentially be found in metal complexes in the diketo, partly or completely hydrolyzed/solvolyzed forms, thus providing a variety of possibilities for coordination chemistry. The crystallographically established coordination modes of (py)CO(py)CO(py) and its forms are shown in Scheme 22.



Scheme 22. The crystallographically established coordination modes of (py)CO(py)CO(py) and its various hydrolyzed/solvolyzed forms with the Harris notations[3] that describe these modes.

Mak and co-workers were the first to study the coordination properties of (py)CO(py)CO(py).[150] $[Cu(NO_3)_2\{(py)CO(py)CO(py)\}]$ (**154**) and $[Cu(H_2O)\{(py)C(OH)_2(py)C(OH)_2(py)\}](NO_3)_2$ (**155**) represent a pair in which the ligand takes the diketo form in the former but is hydrolyzed completely in the latter.[150a] Complexes $[CuCl_2\{(py)CO(py)CO(py)\}]$ (**156**) and $[CuCl\{(py)C(OMe)(OH)C(OMe)(OH)\}]Cl$ (**157**)[150a] constitute another pair in which the ligand remains intact in the former but is solvolyzed at both carbonyl groups in the latter. All forms of the ligand, regardless of whether they are intact, hydrated, or solvated, act in the tridentate *N*,*N*′,*N*′′-chelating mode. Different anion-coordinating abilities lead to two kinds of infinite chains in $\{[Ag\{(py)CO(py)CO(py)\}](ClO_4)\}_n$ (**158**) and $[Ag(NO_3)\{(py)CO(py)CO(py)\}]_n$ (**159**).[150b] In **158**, with a noncoordinating inorganic anion, the ligand takes an *exo,trans* coordination conformation, while in **159**, in which the NO_3^- coordinates to the Ag^I ion, the stereo requirement leads to a *cis*-2.10110 conformation of the ligand (see Scheme 22). In the isomorphous complexes $[Cu^I_2\{(py)CO(py)C(OMe)(OH)(py)\}_2](BF_4)_2$ (**160**) and $[Cu^I_2\{(py)CO(py)C(OMe)(OH)(py)\}_2](ClO_4)_2$ (**161**), the ligand undergoes methanolysis at only one carbonyl group to form its monoketal form, which binds in the 2.100111 mode.[150b] Solvent-controlled reaction between $FeCl_3$ and (py)CO(py)CO(py) yielded four Fe^{III} complexes exhibiting two structural types:[150c] the asymmetric quasi-linear cluster $[Fe_3Cl_2(OMe)_2\{(py)C(OMe)(O)C(OMe)(O)(py)\}_2][FeCl_4]$ (**162**), with a rarely observed eight-coordinate Fe^{III} ion, and the mononuclear complexes $[FeCl_2\{(py)CO(py)C(OH)(O)(py)\}]$ (**163**) and $[FeCl_2\{(py)CO(py)C(OMe)(O)(py)\}]$ (**164**). The ligand is solvolyzed at both carbonyl groups in the trinuclear cluster; the doubly deprotonated form behaves as a 3.2200111 ligand. Hydrolysis/solvolysis occurs at only one carbonyl site in the mononuclear complexes; the monoanionic ligands are tetradentate chelating and adopt the 1.100111 mode.[150c] The $Fe^{III}\cdots Fe^{III}$ exchange interactions in **162** are antiferromagnetic.

Boudalis and co-workers have prepared structurally exciting and magnetically interesting 3d metal clusters.[151] Reaction of excess $Co(O_2CMe)_2{\cdot}4H_2O$ with (py)CO(py)CO(py) in hot DMF gives $[Co^{II}_{20}(DMF)_2(O_2CMe)_{22}(OH)_6\{(py)C(OH)(O)(py)C(O)_2(py)\}_4]$ (**165**). The core (Figure 24) consists of a central double cubane having two missing vertices connected to two warped $\{Co_6O_6\}$ rings through two $\{Co_2O_4\}$ moieties. The triply deprotonated ligands adopt the 6.3221111 and 5.2220111 modes. The Co^{II}_{20} cluster exhibits superparamagnetic relaxation.[151a]

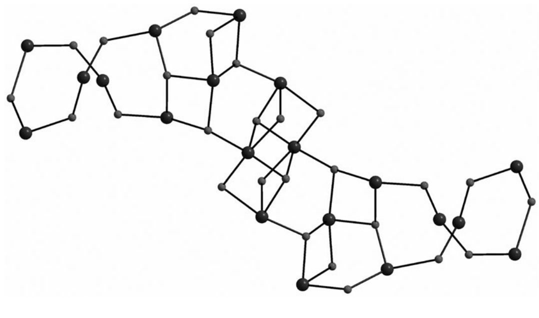


Figure 24. The core of $[Co^{II}_{20}(DMF)_2(O_2CMe)_{22}(OH)_6\{(py)C(OH)(O)(py)C(O)_2(py)\}_4]$ (**165**); only the Co^{II} ions and the monoatomic O bridges are shown.

The pentanuclear cluster $[Cu_5(O_2CMe)_6\{(py)C(OH)(O)(py)C(OH)(O)(py)\}_2]$ (**166**) has been prepared by the reaction of $[Cu_2(H_2O)_2(O_2CMe)_4]$ with (py)CO(py)CO(py) in 10:1 $MeCN/H_2O$.[151b] The Cu^{II} centers are arranged in an "S"-shaped configuration and are bridged by the doubly deprotonated bis(*gem*-diolate) ligands which adopt the 3.2200111 mode, similar to that observed for $(py)C(OMe)(O)C(OMe)(O)(py)^{2-}$ in **162**. Variable-temperature dc magnetic susceptibility data indicate the interplay of both ferro- and antiferromagnetic, intramolecular exchange interactions stabilizing an $S = 3/2$ ground state.

The $[Cu_2(H_2O)_2(O_2CMe)_4]$/(py)CO(py)CO(py) and $Co(O_2CMe)_2{\cdot}4H_2O$/(py)CO(py)CO(py) reaction systems in EtOH and MeOH (in the presence of N_3^- ions) yield clusters $[Cu_4(EtOH)_2(O_2CMe)_5\{(py)C(OEt)(O)C(O)_2(py)\}]$ (**167**) and $[Co_4(N_3)_2(O_2CMe)_2\{(py)C(OMe)(O)(py)C(OMe)(O)\}_2]$ (**168**), respectively.[151c] Complex **167** consists of four Cu^{II} ions in a virtually linear arrangement; bridging between the metal ions is mainly provided by the 4.2220111 $(py)C(OEt)(O)C(O)_2(py)^{3-}$ ligand. It exhibits ferromagnetic couplings among all nearest neighbors and antiferromagnetic next-nearest-neighbor interactions, which stabilize an $S = 1$ ground state. Complex **168** comprises four Co^{II} ions in a defective double-cubane topology bridged by the dianionic bis(hemiketal) form of the ligand, which is found in the 3.2200111 coordination mode, and by 3.300 azido ligands. It exhibits ferromagnetic exchange interactions as a consequence of the end-on azido ligands.

The remarkable cluster $[Ni_5(MeOH)_2(N_3)_4(O_2CMe)_4\{(py)CO(py)C(OMe)(O)(py)\}_2]$ (**169**) has been synthesized by the reaction of excess $Ni(O_2CMe)_2{\cdot}4H_2O$ with (py)CO(py)CO(py) and NaN_3 in refluxing MeOH.[151d] The molecule consists of five Ni^{II} ions in a helical arrangement in which the monoanionic carbonyl-hemiketal ligand adopts the 2.200111 mode. The Ni^{II} ions are ferromagnetically coupled, and the ground state of the complex is $S = 5$. Experiments on ac susceptibility reveal the existence of out-of-phase signals indicative of slow magnetization relaxation. Analysis of the signals shows that they are composite, suggesting more than one relaxation process, while analysis of their magnitudes suggests that not all molecules undergo slow relaxation.

8. Conclusions and Future Directions

The examples given on these pages hopefully serve to emphasize the breadth of the coordination chemistry of, and current interest in, di-2-pyridyl ketone and related ligands. This area of research has a rich past and, in the authors' opinion, a challenging and exciting future. It has something for everyone: from smart organic and inorganic synthetic chemistry to metal complexes (both polynuclear and polymeric) with aesthetically pleasant structures, and from high-spin molecules and single-molecule magnets to single-chain magnets and molecular complexes with interesting optical properties. We hope that the readers are as fascinated as we are by the many ways in which coordination to a metal ion may modify and control the reactivity of organic molecules bearing a ketone group. We have seen that reactivity at the carbonyl groups(s) in an organic ligand may be enhanced upon coordination and a very subtle control over the organic chemistry of the ligand may be exerted. If this Microreview stimulates any reader to delve into the subject of the reactivity of coordinated ligands, it has served its purpose.

The immense structural diversity of many of the metal complexes described stems from the ability of deprotonated ligands that derive from ketone-containing heterocycles to exhibit a great variety of coordination modes [e.g. see Schemes 10 and 22]. Employment of a second or even a third organic, e.g. a carboxylate, or inorganic, e.g. the azido, ligand in this chemistry gives an extraordinary structural flexibility in the resulting mixed-ligand systems ("blends"). The diversity of structures for a given ligand is remarkable, and has prevented up to now any guiding principles from being proposed. The clusters with the fully deprotonated ligands do not seem to correspond in a straightforward manner to polyhedral archetypes or to fragments of common minerals, but display a richness of nuclearities and topologies that appears to be unpredictable but intriguing.

This area of research will undoubtedly continue to expand, given the recent nature of the majority of references in this Microreview and the numerous synthetic routes now documented for the isolation of metal complexes with the ligands described herein. Obvious topics for further investigation include the items listed below.

1. The chemistry of other 3d metals, and second- and third-row transition metals with such ligands: For example, the reactions of V and Cr sources with $(py)_2CO$ and related ligands should be studied in detail, considering how interesting the magnetic properties of the products could be. It is also surprising that Fe^{II} and Fe^{III} complexes have not been investigated much; high-spin Fe^{III} ($S = 5/2$) complexes are promising candidates that can be used to obtain large S values in the ground state.

2. Studies of the chemistry of $(py)_2CO$-related ligands with the oxophilic Ln^{III} ions: Such studies are almost completely lacking and the products may have interesting luminescence properties.

3. Further studies on the chemistry of heterometallic complexes of $(py)_2CO$ and related ligands: For example, 3d/4f metal clusters are rare and, in the context of the discoveries that such complexes can be SMMs, they could be interesting.

4. Investigation of the attack by the nucleophiles described in part 3.5 on the carbonyl groups of (py)COCO(py) and (py)CO(py)CO(py) (Scheme 3): Such investigations could lead to clusters with extremely high nuclearities.

5. Further studies on the coordination chemistry of $(im)_2CO$ and (im)COCO(im) (Scheme 3) with 3d metal ions other than Cu^{II} and with Ln^{III} ions: Reactions of these ligands with metal ions might be extremely useful for the synthesis of novel imidazole- or imidazole/oxalate-containing coordination polymers.

6. The use of new ketone-based ligands in metal chemistry: Synthesizing new ligands will be challenging and may lead to metal complexes with new structural types. Much of the work outlined in this report has involved pyridyl-type ligands, and the results obtained from such studies show the importance of both the electronic and steric effects that the pyridyl groups impart. However, there has been no work carried out on ligands with other donor groups, e.g. phenol groups instead of pyridyl groups; there is certainly significant scope for research with such ligands.

This research is still in its childhood, and we do believe that the future promises many more new and exciting complexes with a host of metal ions.

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