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Cooperative Metal–Ligand Assisted *E/Z* Isomerization and Cyano Activation at Cu^{II} and Co^{II} Complexes of Arylhydrazones of Active Methylene Nitriles

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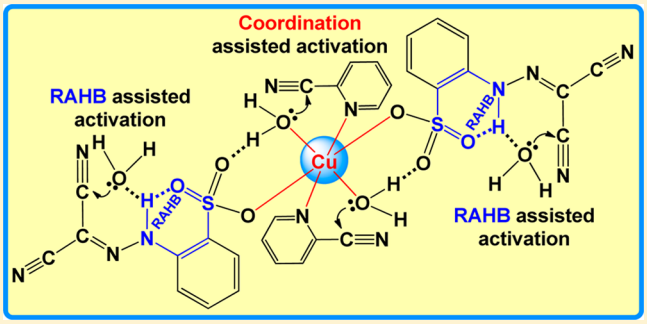
Supporting Information

ABSTRACT: New (*E/Z*)-2-(2-(1-cyano-2-methoxy-2-oxoethylidene)hydrazinyl)benzoic acid (H_2L^4) and known sodium 2-(2-(dicyanomethylene)hydrazinyl)benzenesulfonate ($NaHL^1$), 2-(2-(dicyano-methylene)hydrazinyl)benzoic acid (H_2L^2), and sodium (*E/Z*)-2-(2-(1-cyano-2-methoxy-2-oxoethylidene)hydrazinyl)benzenesulfonate ($NaHL^3$) were used in the template synthesis of a series of Cu^{II} and Co^{II} complexes $[Cu(H_2O)_2L^{1a}]\cdot H_2O$ (**1**), $[Cu(H_2O)(3\text{-pyon})L^{1b}]\cdot H_2O$ (**2**), $[Cu(H_2O)(4\text{-pyon})L^{1b}]$ (**3**), $[Co(H_2O)((CH_3)_2NCHO)(\mu\text{-}L^{2a})]_2\cdot(CH_3)_2NCHO$ (**4**), $[Cu_3(\mu_3\text{-}OH)(NO_3)(CH_3OH)(\mu_2\text{-}X)_3(\mu_2\text{-}HL^3)]$ (**5**), $[Cu(H_2O)(py)L^3]\cdot H_2O$ (**6**), $[Cu(H_2O)_2(\mu\text{-}L^4)]_6\cdot 6H_2O$ (**7**), $[Cu(2\text{-cnpy}^b)_2(L^{1b})_2]\cdot 2H_2O$ (**8**), $[Cu(2\text{-cnpy}^a)_2(L^{1a})_2]\cdot 2H_2O$ (**9**), and $[Cu(H_2O)(4\text{-cnpy})(L^{1a})_2]$ (**10**), where 3-pyon = 1-(pyridin-3-yl)ethanone, 4-pyon = 1-(pyridin-4-yl)ethanone, py = pyridine, HX = *syn*-2-pyridinealdoxime, 4-cnpy = 4-cyanopyridine; 2-cnpy^a, 2-cnpy^b, L^{1a}, L^{1b}, L^{2a} are the ligands derived from nucleophilic attack of methanol (a) or water (b) on a cyano group of 2-cyanopyridine (2-cnpy), L^1 or L^2, respectively, giving the corresponding iminoesters (2-cnpy^a, L^{1a} or L^{2a}) or carboxamides (2-cnpy^b or L^{1b}). An auxiliary ligand, namely *syn*-2-pyridinealdoxime or pyridine, acting cooperatively with the metal ion (Cu^{II} in this case), induced an *E/Z* isomerization of the H_2L^4 ligand; the *E*- and *Z*-isomers were isolated separately and fully characterized (compounds **9** and **10**, respectively). A one-pot activation of nitrile groups in different molecules was achieved in the syntheses of **8** and **9**. Complexes **1**−**10** are catalyst precursors for the solvent-free microwave (MW)-assisted selective oxidation of secondary alcohols to the corresponding ketones, with typical yields in the 29−99% range (TOFs up to 4.94×10^3 h^{-1}) after 30 min of MW irradiation.



1. INTRODUCTION

Malononitriles, such as ylidenemalononitriles, alkylidenemalononitriles, cycloalkylidenemalononitriles, arylidenemalononitriles, as well as other related active methylene nitriles, are well-known versatile reagents. Their chemistry has been well studied[1] but is still attracting considerable interest.[2] The hydrazone moiety is also ubiquitous in various fields ranging from organic transformations[3] and medical applications[4] to coordination[5] and dynamic combinatorial[6] chemistries, metal and covalent organic frameworks,[7] hole-transporting materials,[8] and various dyes,[9] among others.[10] Azocoupling[11] of aryldiazonium salts with active methylene nitriles (for example, malononitrile, methyl 2-cyanoacetate, ethyl 2-cyanoacetate, etc., see below) leads to multifunctionalized arylhydrazones of active methylene nitriles (AAMNs, Scheme 1) of rich reactivity.[2a,5a,12]

Earlier it was demonstrated that resonance-assisted hydrogen bonding [RAHB, X···H−Y ↔ Y···H−X (X, Y = N, O, S, etc.), Scheme 1][13] and/or metal ions (Mn^{II}, Cu^{II}) can promote nucleophilic attack on one or both cyano groups in AAMNs leading to a variety of amidines, carboxamides and imino ethers depending on the nucleophiles and conditions used.[12] It would be worthwhile to further extend this approach (combining both of these possibilities) not only to other metal ions (for instance Co^{II}) but also toward a cooperative action of the metal and an

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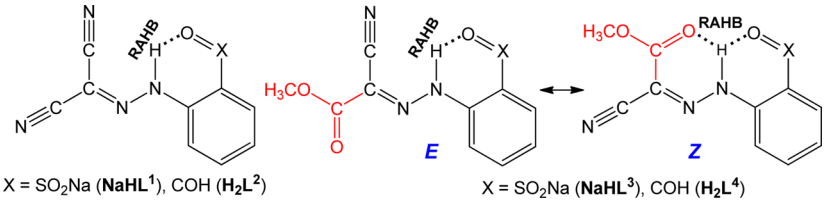
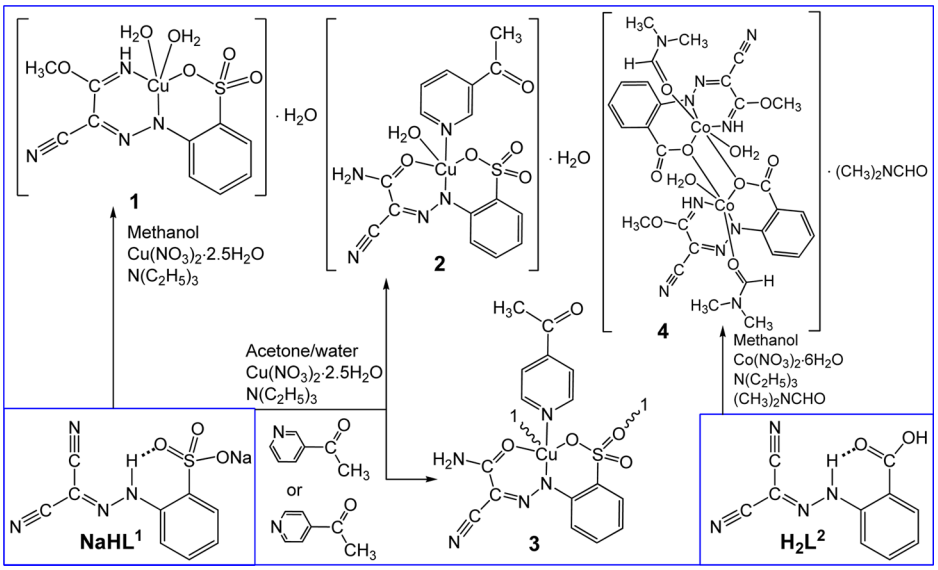
Scheme 1. Arylhydrazones of Active Methylene Nitriles Showing RAHB Sites



Scheme 2. Template Syntheses of 1−4



organic ligand which could be of synthetic value, as recognized in a few other cases of metal−ligand cooperation.[14]

Another aspect of this study concerns the simultaneous one-pot activation of cyano groups which belong to different substrates, for instance 2-cyanopyridine and malononitrile. The separate template transformation of the C≡N group in 2-cyanopyridine[15] or AAMNs[12] upon synthesis of coordination compounds is well-known for different metal centers. However, their concerted activation should widen the toolset of synthetic coordination chemistry, and this approach could be useful, e.g., for the synthesis of multifunctional drugs, cocrystals, supramolecular assemblies with some connotations in catalysis and molecular recognition.[2,6]

Along with their potential in organic and inorganic syntheses, AAMNs are convenient model compounds to study both the enol-azo ⇌ hydrazone tautomeric equilibrium and the *E*/*Z*-hydrazone isomerization (Scheme 1).[16] Generally, the process of *E*/*Z* isomerization, i.e. the interconversion between the *E* and *Z* isomers, occurs readily and can be promoted by temperature, light, change in pH, different solvents, and metal ions,[12c,16,17] thus providing potential applications in analytic and material chemistry, catalysis, etc.[18] Very recently, we have demonstrated that the interplay between RAHB and coordination can also be used for an easy resolution of *E* and *Z* isomers and synthesis of different types of coordination compounds.[18a] Auxiliary ligands play an important role in synthetic coordination chemistry, usually being used to stabilize particular complexes and/or to modify their properties, such as solubility, acidity, buffer capacity, etc., which are important, e.g., for catalytic applications.[5a] However, to our knowledge, auxiliary ligands have not yet been applied to assist the *E*/*Z* isomerization, and this possibility is explored in this work, providing a new case of metal and ligand cooperation in synthesis.

Concerning other possible applications of complexes with the AAMNs ligands, the microwave (MW)-assisted oxidation of alcohols to carbonyl compounds[19] was selected to demonstrate the potential of such complexes in catalysis, since MW-assisted catalytic systems based on copper(II) complexes can show interesting features.[19c,d,20] Moreover, TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) radical, combined with a suitable metal species, is a well-known efficient mediator for oxidation of alcohols,[19,20] and hence it would also be interesting to associate it to the copper(II) complexes derived from AAMNs toward the selective oxidation of alcohols to the corresponding carbonyl compounds.

Hence, on the basis of the above considerations, we focused this work on the following aims: (i) to exploit the metal−ligand cooperation for direct one-pot syntheses of new Co^{II} and Cu^{II} complexes derived from AAMN ligands; (ii) to activate, in one pot, C≡N bonds which belong to different substrates, namely AAMNs and cyanopyridines; (iii) to use an auxiliary ligand to regulate the *E*/*Z* isomerization of the AAMN ligands upon their coordination; (iv) to evaluate the catalytic activity of the prepared new complexes in the model MW-assisted and TEMPO-mediated solvent-free peroxidative oxidation of 1-phenylethanol to acetophenone.

RESULTS AND DISCUSSION

Template Synthesis and Characterization of New Cu^{II} and Co^{II} Complexes. Several known AAMNs, namely sodium 2-(2-(dicyanomethylene)hydrazinyl)benzene sulfonate

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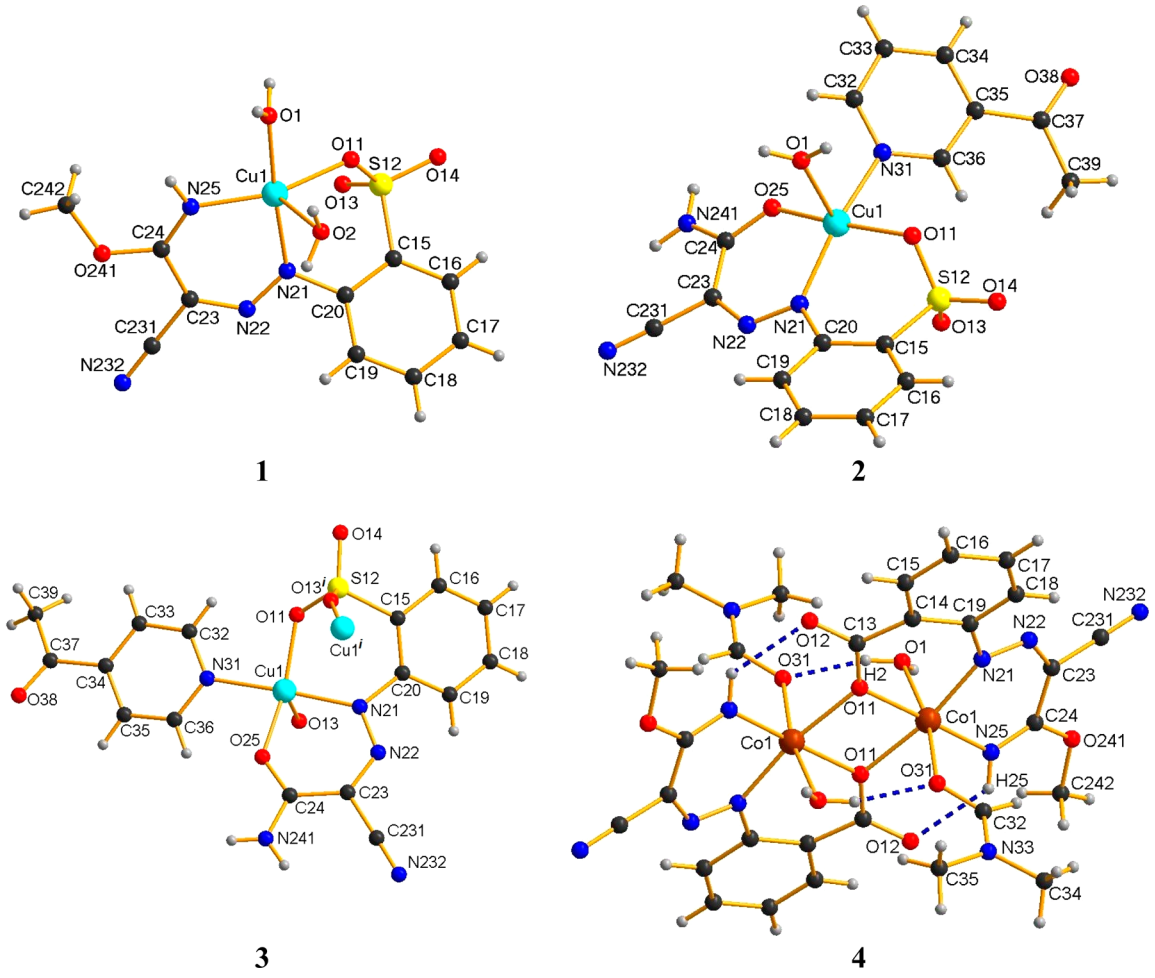

Figure 1. X-ray molecular structures of complexes **1**–**4** with atom numbering schemes. **1** and **2** are monomers, **3** forms a 1-D polymer with molecules bridged through O(13), **4** is a centrosymmetric dimer. Solvent molecules in **1**, **2**, and **4** are omitted for clarity. Intramolecular hydrogen bonds in **4** are shown as dotted lines.

(NaHL^1),[12c] 2-(2-(dicyanomethylene)hydrazinyl)benzoic acid (H_2L^2),[12a,c] sodium (*E*/*Z*)-2-(2-(1-cyano-2-methoxy-2-oxoethylidene)hydrazinyl)benzenesulfonate (NaHL^3)[18a] and the new (*E*/*Z*)-2-(2-(1-cyano-2-methoxy-2-oxoethylidene)-hydrazinyl)benzoic acid (H_2L^4) were used as starting materials in the template synthesis of new coordination compounds. H_2L^4 exists in DMSO solution as a mixture of the two isomeric *E*- and *Z*-hydrazone forms, the former involving a two-centered RAHB system, and the latter, a three-centered one (Scheme 1); the ^{1}H NMR shifts of the N–H···O proton, characteristic of the two- and three-centered RAHB systems, are observed at δ 13.10 and 14.59, respectively. The mole ratio of the isomers has been determined by the relative integration of the NH signals in the ^{1}H NMR spectrum, being 55% for the *E*-isomer and 45% for the *Z* one (see Figure S1 in Supporting Information [SI]). The ^{13}C{^{1}H} NMR spectrum (in DMSO-d_6) of H_2L^4 exhibits two sets of peaks, accounting for the mixture of the *E*- and *Z*-hydrazone forms (see Figure S2 in SI). The IR spectrum of H_2L^4 shows ν(OH), ν(NH), ν(C=N), and ν(C=N) vibrations at 3475 and 3134, 2962 and 2885, 2238 and 2210, 1606, and 1589 cm^{-1} respectively, while the ν(C=O) signals of the free and H-bonded carbonyl groups are observed at 1710 (*E*-hydrazone) and 1669 (*Z*-hydrazone) cm^{-1}, respectively, also supporting the existence of both isomers in the solid state. Elemental analysis and the ESI-MS peak at 248.2 $[Mr + H]^+$ are also consistent with the structure of H_2L^4.

The AAMNs possess a strong RAHB system. However, it is weakened by addition of a base which increases the lability of the N–H bond and promotes the coordination.[18a] Thus, the reactions of $Cu(NO_3)_2{\cdot}2.5H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ with NaHL^1 and H_2L^2, respectively, in methanol or water, were performed in the presence of triethylamine as a base, whereas 3-pyon = 1-(pyridin-3-yl)ethanone and 4-pyon =1-(pyridin-4-yl)ethanone were used as auxiliary ligands. As a result, the Cu^{II} and Co^{II} complexes $[Cu(H_2O)_2L^{1a}]{\cdot}H_2O$ (**1**), $[Cu(H_2O)(3\text{-pyon})L^{1b}]{\cdot}H_2O$ (**2**), $[Cu(H_2O)(4\text{-pyon})L^{1b}]$ (**3**), and $[Co(H_2O)((CH_3)_2NCHO)(\mu\text{-}L^{2a}]_2{\cdot}(CH_3)_2NCHO$ (**4**) (where L^a and L^b are the iminoester and carboxamide forms of L derived upon reaction of one of the nitrile groups with CH_3OH and H_2O solvent, respectively) (Scheme 2) were isolated and characterized by elemental analysis, ESI-MS, IR spectroscopy, and single-crystal X-ray diffraction.

The nuclearity and type of structure of the formed complexes depend on the AAMN pro-ligand, metal ion (Cu^{II} or Co^{II}), auxiliary ligand (3-pyon or 4-pyon), and nucleophile (methanol or water) used for the reaction (Scheme 2). In the template synthesis, one of the C≡N groups of the starting AAMN, activated by the metal ion, undergoes nucleophilic attack by the protic solvent (methanol or water), converting to a ligated

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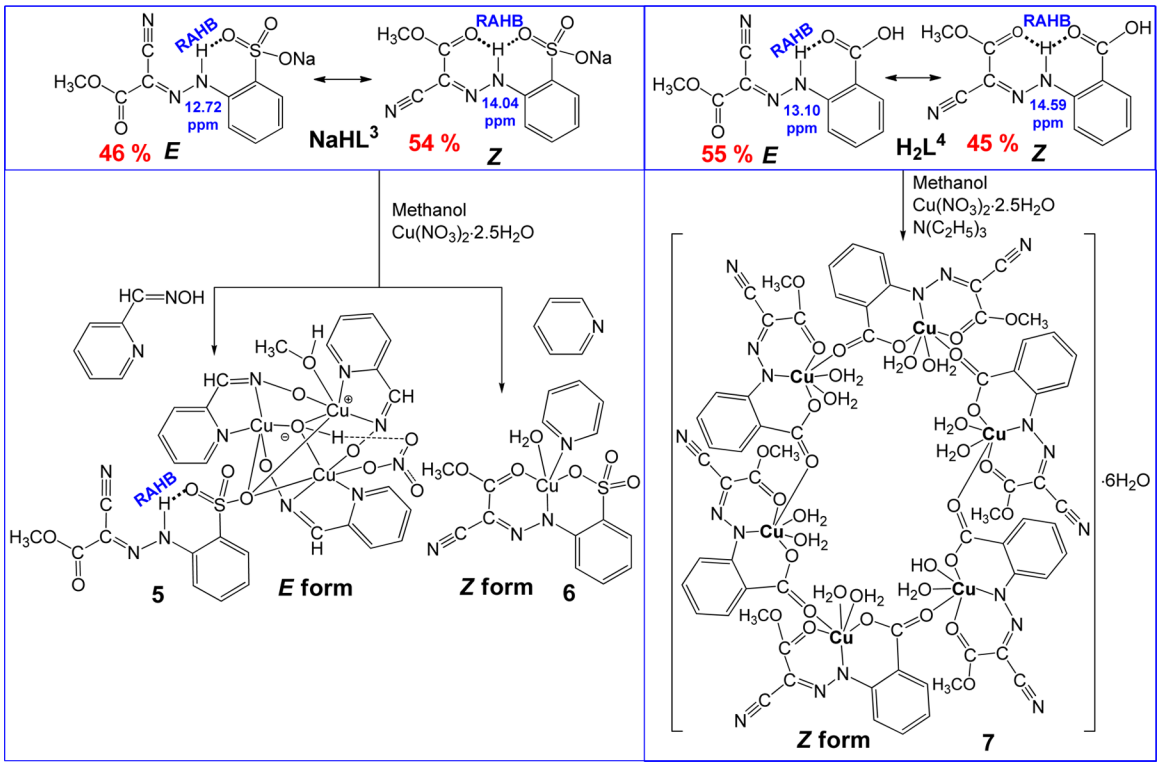
Scheme 3. *E*/*Z* Isomerization of AAMN Ligands in the Synthesis of 5−7



iminoester or carboxamide, respectively. The other cyano moiety remains uncoordinated and thus unactivated. In the IR spectra of **1**−**4**, ν(OH) and ν(NH) vibrations are observed in the ∼3415−3195 cm^{-1} range, while ν(C≡N) of the unreacted cyano group appears at 2212, 2202, 2203, and 2209 cm^{-1}, respectively. Elemental analysis and ESI-MS support the formulation of **1**−**4**, while the structures are confirmed by X-ray diffraction analyses (see Figure 1 and Tables S1−S3 in SI).

The crystal structures are shown in Figure 1 together with the atomic numbering schemes. Molecular dimensions are compared in Table S2 in the SI. In **1**, the copper atom is five-coordinate being bonded to a tridentate ligand with donor atoms, a N-hydrazone atom N21 at 1.976(3) Å, a sulfonyl oxygen atom O11 at 1.988(2) Å, and a nitrogen atom N25 from the iminoester of the L[1a] ligand at 1.922(3) Å. The equatorial plane is completed by a water molecule O1 at 2.005(3) Å. Another water molecule in the axial position at 2.317(3) Å completes the square pyramidal environment (τ_5 = 0.28).[21] The metal atom in **2** has a similar structure, but the terdentate ligand contains a carboxamide moiety of the L[1b] ligand, bond lengths being Cu−O11 1.977(3), Cu−N21 1.992(3), Cu−O25 1.922(3) Å. The equatorial plane is completed with 3-pyon ligand bonded through nitrogen N31 at 2.032(3) Å while a water molecule in an axial position at 2.233(3) Å completes the square pyramidal environment (τ_5 = 0.07).[21]

The structure of **3** is a one-dimensional (1D) polymer. Each copper atom is bonded to the same terdentate L[1b] ligand as in **2** with dimensions Cu−O11 1.962(3), Cu−N21 1.976(3), Cu−O25 1.908(3) Å. The equatorial plane is completed by a nitrogen atom N31 from a 4-pyon ligand at 2.048(3) Å. The copper cation presents a value of 0.22 for the τ_5 parameter,[21] suggesting a distorted square pyramidal geometry. For this structure, however, unlike **2**, there is no water molecule, and instead the axial position is occupied by a sulfonyl oxygen atom O13 (1/2 − *x*, −1/2 + *y*, 1/2 − *z*) from an adjacent molecule at 2.286(3) Å, thus forming a 1D polymer along the screw axis in the *b* direction.

For both complexes **2** and **3**, the chelating ligand displays the carboxamide form, $H_2NC(=O)-$, rather than the iminol one, $HN=C(-OH)-$, conceivably on account of the conjugation effect at the six-membered metallacycle in the former case.

In **4**, the cobalt atom is six-coordinate with a distorted octahedral environment being bonded to a terdentate L[2a] ligand with donor atoms, a N-hydrazone atom N21 at 1.997(6) Å, a nitrogen atom N25 from the iminoester at 1.965(3) Å and a carbonyl oxygen atom O11 at 2.012(4) Å. The equatorial plane is completed via the oxygen atom O11 (1 − *x*, 1 − *y*,1 − *z*) at 2.092(4) Å across a center of symmetry, thus forming a dimer. In axial positions are a water molecule O1 at 2.136(5) Å and an oxygen atom O31 from dimethylformamide solvent at 2.114(4) Å.

In **1**−**4** the N−N, C=N, C=NH, and C=O bond lengths of 1.290(4)−1.312(8), 1.314(5)−1.329(9), 1.278(4)−1.279(8), and 1.255(4)−1.260(4) Å (see Table S2 in SI) provide evidence for electron delocalization in the six-membered rings. The crystal structures of **1**−**4** are stabilized by hydrogen-bonding interactions between the coordinated and uncoordinated solvent hydrogens and the amino, imino, ketone, carboxyl, and sulfonyl groups in adjacent units (see Table S3 in SI). Moreover, two intramolecular hydrogen bonds between the two halves of the dimer are formed, namely, O1−H2···O31 (1 − *x*, 1 − *y*, 1 − *z*) [2.766(6) Å] and N25−H25···O12 (1 − *x*, 1 − *y*, 1 − *z*) [2.825(7) Å], which are derived from the interaction of the coordinated imino hydrogen and free carboxylic oxygen and the hydrogen atom of coordinated water molecule and the oxygen atom of coordinated dimethylformamide in **4** (Figure 1).

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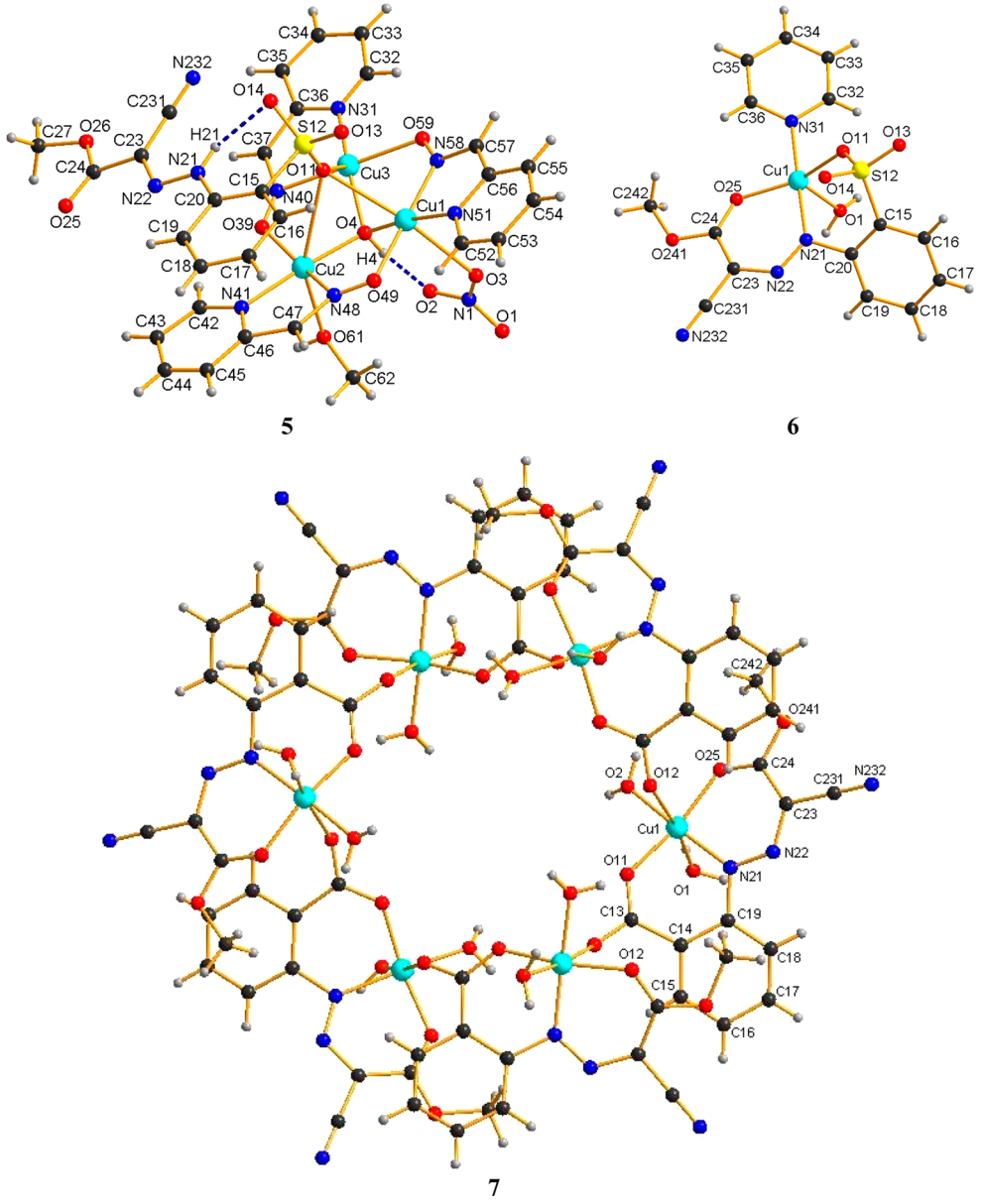

Figure 2. X-ray molecular structures of **5**, a trinuclear complex, **6**, a mononuclear complex, and **7**, a hexanuclear complex with crystallographic −3 symmetry, together with the atom numbering systems. The central cavity in **7** is occupied by disordered solvent water molecules (not shown).

Auxiliary Ligand-Assisted *E/Z* Isomerization. It is well-known[18a] that $NaHL^3$ exits in DMSO solution as a mixture of the *E*- and *Z*-hydrazone isomeric forms (Scheme 3). The ortho-carboxyl substituted analogue of $NaHL$,[3] namely H_2L,[4] also exists as an *E/Z*-hydrazone mixture with comparable amounts of both forms, as indicated by the ^{1}H NMR data (Scheme 3). It should be noted that with the increase of the electron-withdrawing ability of the substituent in the phenyl ring of AAMN from $-SO_3^-$ (in $NaHL^3$) to −COOH (in H_2L^4) (Hammett's σ_p = 0.35 or 0.45, respectively;[22] σ_o = 0.23 or 0.29, respectively, where $\sigma_o = 0.65 \cdot \sigma_p$[22e]) the *E*↔*Z* balance shifts to the *E*-hydrazone form (Scheme 3). This can be explained by the higher promotion of the NH acidity by the −COOH group in comparison to $-SO_3^-$.

Various factors can shift the *E/Z* equilibrium,[12c,16,17,18a] and for instance, it was found very recently[18a] that resolution of *E* and *Z* isomers can be achieved by interplay between RAHB and coordination bonds. In the current work, we demonstrate that auxiliary ligands can also assist the *E/Z* isomerization or resolution. In fact, the reaction of $Cu(NO_3)_2 \cdot 2.5H_2O$ with $NaHL^3$ in the presence of *syn*-2-pyridinealdoxime (HX) or pyridine (py), in methanol, leads to $[Cu_3(\mu_3\text{-}OH)(NO_3)(CH_3OH)(\mu_2\text{-}X)_3(\mu_2\text{-}HL^3)]$ (**5**) (*E*-hydrazone) and $[Cu(H_2O)(py)L^3] \cdot H_2O$ (**6**) (*Z*-hydrazone), respectively (Scheme 3). Moreover, the new hexanuclear copper(II) complex $[Cu(H_2O)_2(\mu\text{-}L^4)]_6 \cdot 6H_2O$ (**7**) was obtained upon *E/Z* → *Z* conversion by reaction of the *E/Z*-isomeric mixture of H_2L^4 with $Cu(NO_3)_2 \cdot 2.5H_2O$, in methanol, in the absence of an auxiliary ligand but in the presence of the base $N(C_2H_5)_3$ (Scheme 3). These compounds **5**−**7** have been isolated as air-stable crystalline solids and characterized by IR spectroscopy, ESI-MS, elemental analysis, and X-ray crystallography.

The IR spectra of the isolated complexes exhibit $\nu(C{\equiv}N)$ at 2218, 2220, and 2219 cm^{-1} for **5**, **6**, and **7**, respectively, while in the starting materials they are observed at 2209 cm^{-1} for $NaHL^3$ and at 2238 and 2210 cm^{-1} for H_2L^4. The absorptions

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at 1656 and 1709 cm^{-1} can be assigned to ν(C═O) in **6** and **7**, respectively. Elemental analysis and ESI-MS data also support the structures of **5**−**7**. Thus, the methanol solutions of **5**, **6**, and **7** display, by ESI-MS, parent peaks at m/z = 853.2 $[Mr - NO_3 - CH_3OH]^+$, 442.8 $[Mr + H]^+$, and 345.7 $[Mr - H_2O + H]^+$, respectively. Under the ESI-MS conditions, complexes **5** and **7** lose coordinated solvent molecules and the nitrate ligand (in **5**), while the hexanuclear **7** decomposes to mononuclear fragments.

$NaHL^3$ exists as a mixture of *E,Z*-isomers (46% *E* and 54% *Z*) in dimethyl sulfoxide solution, but the isomeric equilibrium is pH dependent.[18a] In fact, the *E,Z* → *E* resolution occurs in acidic medium, while in basic medium the reverse *E,Z* → *Z* conversion is observed.[18a] In accord, the presence of *syn*-2-pyridinealdoxime with an acidic character (pK_1 = 3.59)[23] promotes the formation of the *E*-isomer in complex **5**, whereas the basic character of pyridine or triethylamine favors the *Z* form in compounds **6** and **7** (Scheme 3).

Light-green and dark-green crystals of the complexes $[Cu_3(\mu_3\text{-}OH)(NO_3)(CH_3OH)(\mu_2\text{-}X)_3(\mu_2\text{-}HL^3)]$ (**5**) and $[Cu(H_2O)(py)L^3]\cdot H_2O$ (**6**), suitable for X-ray diffraction analysis, were prepared from $Cu(NO_3)_2\cdot 2.5H_2O$ and $NaHL^3$, in the presence of HX = *syn*-2-pyridinealdoxime and py = pyridine, respectively, in methanol, whereas dark-green crystals of $[Cu(H_2O)_2(\mu\text{-}L^4)]_6\cdot 6H_2O$ (**7**) were obtained from methanol solution of $Cu(NO_3)_2\cdot 2.5H_2O$, H_2L^4 and $N(C_2H_5)_3$. The structures are shown in Figure 2, and selected interatomic distances and angles and hydrogen-bonding interactions are listed in Table S2 and S3 in the SI respectively.

In the trinuclear complex **5**, Cu(1) is six-coordinate with a distorted octahedral geometry, while Cu2 and Cu3 are five-coordinate with distorted square pyramidal (τ_5 = 0.25)[21] geometries. The coordination positions are occupied by three deprotonated *syn*-2-pyridinealdoximate ligands (X^-), together with one each of $(HL^3)^-$, NO_3^-, OH^-, and CH_3OH. All three metal atoms are strongly bonded to two nitrogen atoms from one X^-, an oxygen from another X^-, and a bridging hydroxide O4 in an equatorial plane, though with differing axial atom(s). Cu1 shows four strong bonds in the equatorial plane with N51, N58 from X^- at 1.996(6), 1.904(8) Å, O49 from a second X^- at 2.029(6), and the bridging hydroxide O4 at 1.960(4) Å. There are two weak bonds in axial positions a sulphonyl oxygen O11 at 2.539(5) Å (which is also weakly bonded to Cu3), and a nitrate oxygen O3 at 2.653(7) Å. Cu2 is bonded to N41 and N48 from the second X^- at 2.044(7) and, 1.965(7) Å, O39 from a third X^- at 2.020(6) Å, and the bridging hydroxide O4 at 1.936(5) Å; in addition there is a weak bond in the axial site to O61 from a solvent methanol at 2.359(5) Å. Cu3 is bonded to N31, N38 from the third X^- at 1.924(7), 2.056(8) Å, O59 from the first X^- at 2.181(5) Å and the bridging oxygen O4 at 1.940(5) Å. The distorted square pyramidal structure is completed by the sulphonyl oxygen O11 in an axial position at 2.436(5) Å. Thus, all three X^- ligands bond to one copper through two nitrogen atoms and to another copper through the oxygen, while $(HL^3)^-$ bridges two copper ions weakly in axial positions through one sulphonyl oxygen atom O11 leaving the rest of the ligand free. The Cu1···Cu2, Cu1···Cu3, and Cu2···Cu3 distances are 3.147(1), 3.088(1), and 3.171(1) Å, respectively.

There are also two intramolecular hydrogen bonds in the trinuclear complex. The hydroxyl which bridges the three copper atoms forms a donor hydrogen bond to the nitrate, O4−H4···O2 at 2.711(7) Å. The second hydrogen bond is within the HL^{3-} ligand, namely, N21−H21···O14 at 2.740(7). Extensive intermolecular H-bond interactions (Table S3 in the SI), linking the coordinated methanol molecule (acting as donor) and the NO_3^- ligand (acting as acceptor), with the O61−H61···O1 distance of 2.750(7) Å, are another interesting feature of the structure.

In complex **6** the Cu ion is in a square pyramidal environment (τ_5 = 0.40),[21] similar to that found in **2**, with an equatorial plane containing two O and one N atoms [O11, O25, and N21] from $(L^3)^{2-}$ at 1.964(4), 1.978(4), 1.993(4) Å and the N31 atom of pyridine at 2.004(4) Å; the apical position is filled by O1 of ligated water at 2.226(4) Å. The crystal structure in **6** is stabilized by medium-strong intermolecular hydrogen bonding interactions (Table S3 in the SI) between the coordinated water molecule and the nitrile or sulfonate bridging groups; the O1−H2···N232 and O1−H1···O23 donor−acceptor distances are 2.879(7) and 2.748(6) Å, respectively.

In the hexanuclear complex **7** (Figure 2) each copper ion has a distorted octahedral coordination geometry with strong bonds in the equatorial plane and weak bonds in axial positions. The $(L^4)^{2-}$ ligand coordinates the Cu^{II} ion in the equatorial plane via the carboxylate oxygen O11 and the ester oxygen O25 and the deprotonated N21 of the hydrazone moiety at distances of 1.964(4), 1.978(4), 1.993(4) Å. The equatorial plane is completed by a water molecule O2 at 1.956(6) Å. The axial sites are occupied by a water molecule O1 at 2.511(6) Å and an oxygen atom O12 of the carboxylate group ($x - y$, x, $1 - z$) from a neighboring molecule at 2.721(6) Å, thus forming a bridge which leads to a hexanuclear complex with crystallographic −3 symmetry. The complex forms a cavity (Figure 2) within which are found disordered water molecules.

This weak Cu1−O12 bond is consistent with the decomposition of **7** in solution into mononuclear fragments, as indicated by ESI-MS (see above).

The copper ion forms two fused six-membered metallacycles, Cu1-O11-C13-C14-C19-N21 and Cu1-O25C24C23-N22N21. Consistent with electron delocalization in these metallacycles are the N22−N21, C23═N22, and C24═O25 bond lengths of 1.308(9), 1.349(9), and 1.224(9) Å (see Table S2 in SI), respectively. The average H_2O···O and H_2O···N distances of the hydrogen bonds in **7** fall within the 1.96(4)−2.21(5) Å range (Table S3 in the SI), consistent with strong hydrogen bonding.

Simultaneous Activation of Nitrile Groups in AAMN and Cyanopyridine. RAHB-assisted nucleophilic attacks on the cyano moieties in AAMNs lead to a variety of amidines, carboxamides, and iminoesters depending on the nucleophiles and conditions used.[12b] Metal centers (e.g., of Mn^{II},[12a] Cu^{II}, or Co^{II} see above) can promote such nucleophilic additions, e.g., of water or alcohol molecules to a cyano group to give a carboxamide or an iminoester, respectively. It is also known that the coordination of 2-cyanopyridine to Ni^{II} or Cu^{II} atom facilitates the nucleophilic addition of a solvent molecule (water, methanol, ethanol) to the cyano group.[15] In this work, a combination of both "activating tools", RAHB and metal center, led to the one-pot activation of C≡N bonds in both 2-cyanopyridine and AAMNs (Scheme 4).

Thus, the reaction of $Cu(NO_3)_2\cdot 2.5H_2O$ with $NaHL^1$ in the presence of triethylamine and 2- or 4-cyanopyridine (2-cnpy or 4-cnpy, respectively) in methanol or water−acetone mixture leads to the Cu^{II} complexes $[Cu(2\text{-}cnpy^b)_2(L^{1b})_2]\cdot 2H_2O$ (**8**), $[Cu(2\text{-}cnpy^a)_2(L^{1a})_2]\cdot 2H_2O$ (**9**), $[Cu(H_2O)(4\text{-}cnpy)(L^{1a})_2]$

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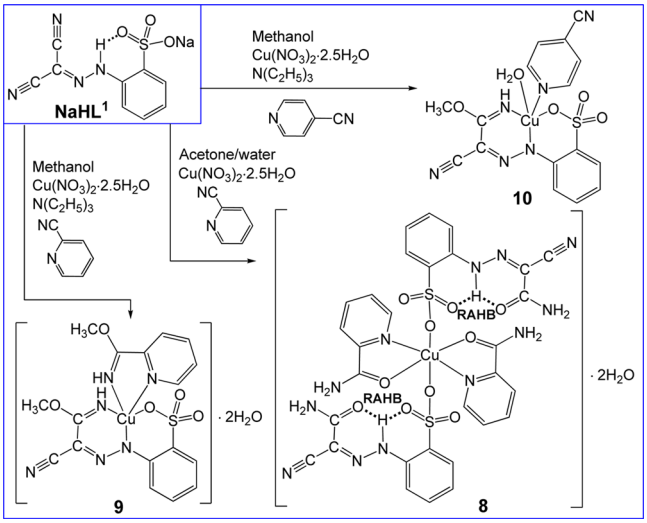
Scheme 4. Coordination and RAHB-Promoted Simultaneous Activation of Two Nitrile Groups in the Syntheses of 8−10



(**10**), where 2-cnpy[b], 2-cnpy[a], L[1b], and L[1a] are the ligands derived from nucleophilic attack of water (b) or methanol (a) solvent on a cyano group of 2-cyanopyridine (2-cnpy) or L[1], giving the corresponding carboxamides (2-cnpy[b] or L[1b]) or iminoesters (2-cnpy[a] or L[1a]) (Scheme 4, Figure 3). In such reactions, water (in **8**) or methanol (in **9**) played the role of a protic nucleophile to both the cyano group of 2-cyanopyridine and one of the cyano groups of L[1]. Under the same reaction conditions, 4-cyanopridine does not undergo nucleophilic attack (the cyano group in the para position does not react), and simply coordinates as such (complex **10**), in contrast to the case of 2-cyanopyridine (complexes **8** and **9**). This difference of reactivity is explained below.

All the obtained complexes **8**−**10** were characterized by elemental analysis, ESI-MS, IR spectroscopy, and single-crystal X-ray diffraction. The ESI-MS$^+$ peaks at 844.3 $[Mr - 2H_2O + H]^+$, 480.9 $[Mr - 2H_2O + H]^+$ or 466.9 $[Mr + H]^+$ support the corresponding formulations, while the IR spectra reveal ν(O−H), ν(N−H), ν(C≡N), and ν(C=N) vibrations at 3201−3455, 2677−3074, 2213−2227, and 1674−1576 cm^{-1}, respectively.

The structure of **8** is centrosymmetric with the Cu^{II} atom in a distorted octahedral geometry being bonded to two bidentate 2-cnpy[b] ligands with Cu1−N31 at 1.968(2) Å and Cu1−O39 at 1.981(2) Å in an equatorial plane and two monodentate ligands L[1] bonded through O(11) at 2.401(2) Å (Scheme 4, Figure 3). The positive charge on copper(II) is neutralized by the negative charges of the sulfo groups. The bifurcated RAHB system N21−H21···O14 and N21−H21···O24 remains intact, with

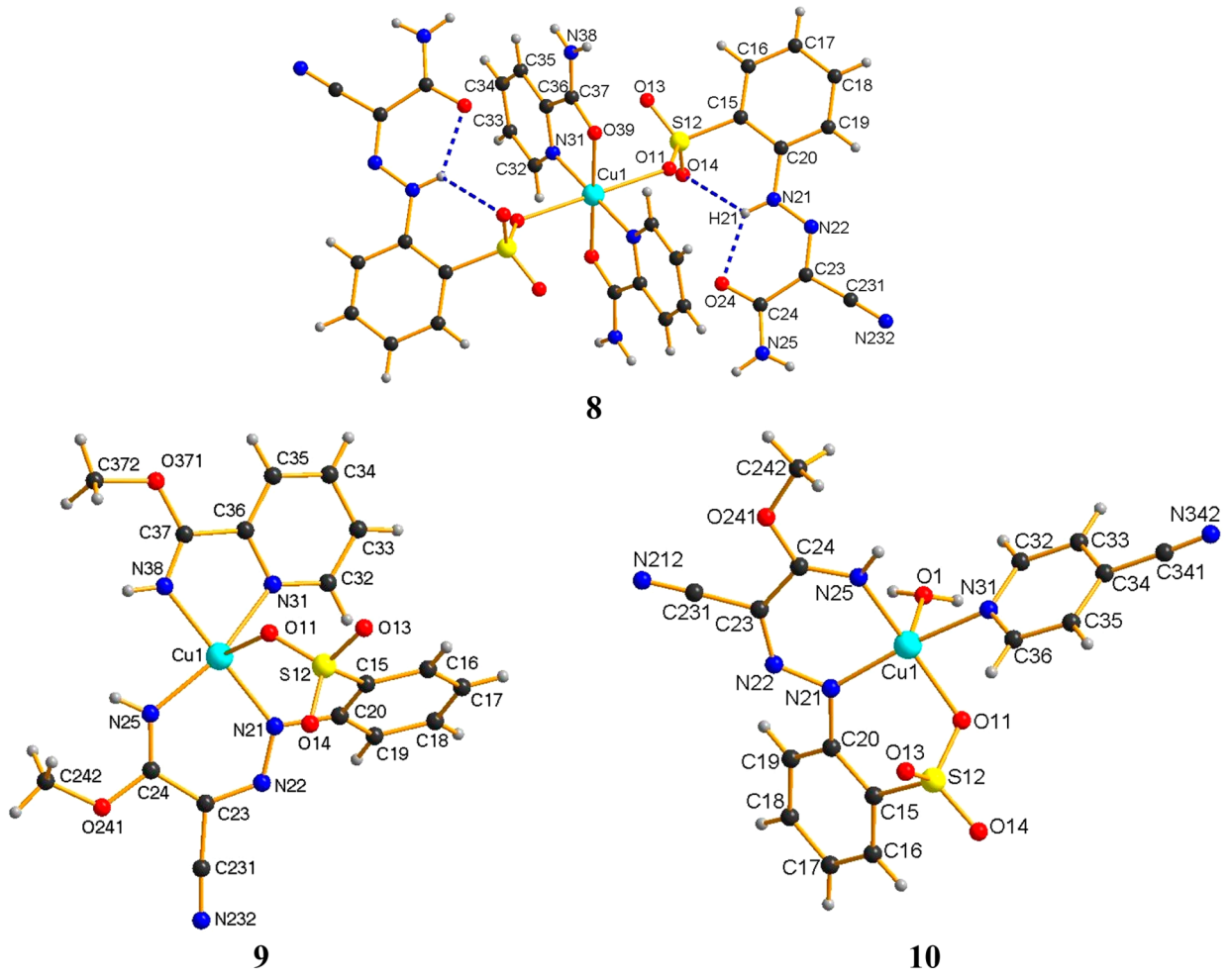


Figure 3. X-ray molecular structures of complexes **8**−**10** with atom numbering schemes. The solvent water molecules in **8** and **9** are omitted for clarity. **8** contains a crystallographic center of symmetry at the metal center. Hydrogen bonds are shown as dotted lines.

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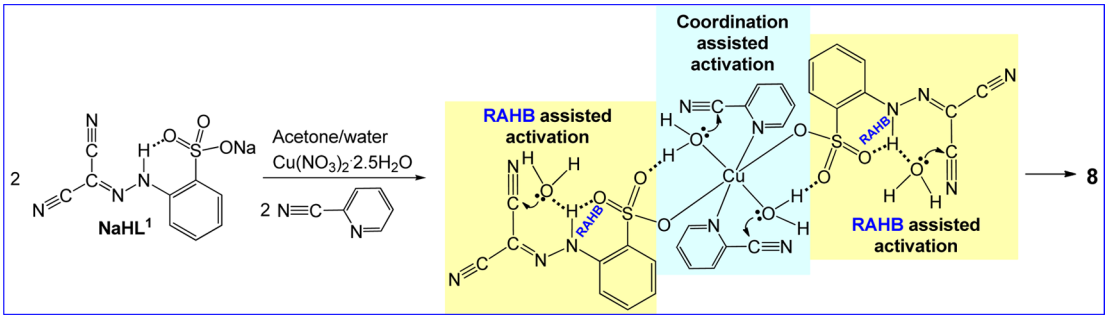
Scheme 5. Proposed Pathway for the Coordination and RAHB-Assisted Activation of Nitriles



N···O distances of 2.958(3) and 2.652(2) Å, respectively, which are longer than the average N···O distance range, 2.538−2.603 Å, observed for other arylhydrazones of active methylene compounds,[9b−d] and indicates a low delocalization within the heterodienic moiety. The N−H···O angles of 119 and 131° (Table S3 in the SI) significantly differ from the average O−H···O angle (149°)[13c] of *β*-diketone enols involved in similar intramolecular RAHB. Moreover, the crystal structure of **8** shows strong intermolecular hydrogen-bond interactions via the uncoordinated amino group and water molecules, as well as oxygen atoms of the sulfo group (Table S3 in the SI).

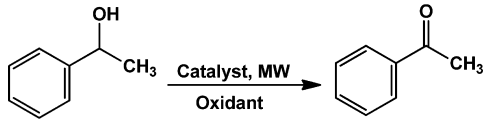
In both complexes **9** and **10** (Figure 3), Cu^{II} is five coordinate with a square pyramidal geometry (τ_5 = 0.41 and 0.12, respectively).[21] In **9**, the equatorial plane is occupied by a bidentate 2-cnpy with N31, N38 at 2.163(4), 1.965(3) Å and two nitrogen atoms N21, N25 of the L^{1a} ligand at 1.965(4), 1.968(4) Å, while a sulphonyl oxygen O11 of this ligand occupies the axial position at 2.222(4) Å. This *fac* arrangement of the terdentate L^{1a} ligand is therefore very different from that found in complexes **1**, **2**, and **3** where the three donor atoms form a *mer* arrangement around the metal. In **10**, the equatorial plane is occupied by the terdentate L^{1a} ligand, now with the familiar *mer* arrangement with O11, N21, N25 at 1.993(2), 1.990(2), 1.941(2) Å together with the pyridine nitrogen N31 at 2.036(2)Å. A water molecule O1 is in the axial position at 2.257(2) Å.

In **9** and **10**, the N21−N22, C23−N22 distances in the six-membered hydrogen-bonded cycles are of 1.295(6), 1.316(6) and 1.304(2), 1.326(3) Å respectively. The imino C24═N25 bonds in **9** and **10** and C43═N41 in **9** are 1.258(7), 1.263(7), and 1.288(3) Å, respectively, which are typical for the C_{sp2}═N bonds. Both crystal structures are stabilized by strong hydrogen-bonding interactions between the coordinated water hydrogens and sulfo, imino (in **9** and **10**), and ketone (in **8**) groups in adjacent units (Table S3 in the SI).

The proposed pathway for the activation of the cyano groups in distinct substrates (Scheme 5 in the case of **8**) is probably initiated by coordination of the sulfo group of HL^1 and the nitrogen atom of 2-cyanopyridine to Cu^{II}. Coordination of water not only allows the formation of an intramolecular hydrogen-bonding system but also approaches the C≡N group of the coordinated 2-cyanopyridine, thus favoring the nucleophilic attack of water to the cyano carbon to produce the ligated carboxamide moiety. Moreover, the RAHB involving another H_2O molecule and the HL^1 ligand (Scheme 5) can assist the nucleophilic attack of water on a cyano group of HL^1, similarly to a mechanism described earlier.[12b] As a result, compound **8** is formed where the newly formed RAHB cycles stabilize the generated amide ligand L^{1b} (Scheme 4). In the synthesis of **9**, in methanol, the base $N(C_2H_5)_3$ would deprotonate the hydrazone unit of AAMN, allowing the Cu^{II} ion to accept the NO chelating moiety. Then two methanol molecules act as protic nucleophiles to cyano groups of both ligated 2-cnpy and L^1 to give the corresponding iminoester ligands (Scheme 4).

Catalytic Activity of 1−10 in Microwave-Assisted Oxidation of Alcohols to Carbonyl Compounds. Complexes **1**−**10** were tested as catalyst precursors for the solvent-free microwave (MW)-assisted oxidation of secondary alcohols (1-phenylethanol was chosen as a model substrate) to ketones with aqueous *tert*-butylhydroperoxide (Bu^tOOH, TBHP) under low power (10 W) MW irradiation (Scheme 6). Selected results are presented in Table 1.

Scheme 6. Solvent-Free MW-Assisted Oxidation of 1-Phenylethanol to Acetophenone



Under typical solvent- and additive-free conditions all the compounds exhibited catalytic activity for the above reaction, leading to yields (based on the alcohol) of acetophenone in the range of 10−31% after 15 min of irradiation (Table 1). The catalyst precursors **2**, **4**−**6** were highly active [TOFs up to 3.2 × 10^3 h^{-1} (**2**), Table 1] under the used conditions. Moreover, a high selectivity toward the formation of acetophenone was observed, since no traces of byproducts were detected by GC−MS analysis of the final reaction mixtures (only the unreacted alcohol was found, apart from the ketone). Blank tests (in the absence of any catalyst precursor) were performed under common reaction conditions, and no significant conversion was observed.

The activity of **1**−**10** in the peroxidative (with *tert*-butylhydroperoxide) oxidation of 1-phenylethanol was also studied in the presence of 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO).[19,20] The TEMPO additive provided a significant increase in the yield of acetophenone (Table 1, Figure 4) under the same reaction conditions. Almost quantitative yields of acetophenone were obtained after only 30 min of MW irradiation, in the presence of the Cu^{II} **2** and **5** (99%, entries 4 and 10, Table 1), and Co^{II} **4** (98%, entry 8, Table 1) compounds. Considering the nuclearities of the catalyst precursors, we may conclude that the mononuclear **2** and **6** were the most effective under the used conditions. Moreover, the presence of N-donor ligands (pyridine or a derivative) in

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Table 1. MW-Assisted Solvent-Free Oxidation of 1-Phenylethanol Using 1−10 As Catalyst Precursors

entry	catalyst precursor	additive (mol % vs substrate)	reaction time (h)	yield[b] (%)	TON [TOF (h^{-1})][c]
1	**1**	–	0.25	9.8	2.45×10^2 (9.79×10^2)
2		TEMPO (2.5)	0.50	28.5	7.13×10^2 (1.43×10^3)
3	**2**	–	0.25	31.2	7.80×10^2 (3.12×10^3)
4		TEMPO (2.5)	0.50	98.6	2.47×10^3 (4.93×10^3)
5	**3**	–	0.25	17.2	4.26×10^2 (1.70×10^3)
6		TEMPO (2.5)	0.50	55.3	1.38×10^3 (2.76×10^3)
7	**4**	–	0.25	31.1	7.77×10^2 (3.11×10^3)
8		TEMPO (2.5)	0.50	97.9	2.45×10^3 (4.90×10^3)
9	**5**	–	0.25	30.6	7.66×10^2 (3.06×10^3)
10		TEMPO (2.5)	0.50	98.8	2.47×10^3 (4.94×10^3)
11	**6**	–	0.25	30.2	7.56×10^2 (3.02×10^3)
12		TEMPO (2.5)	0.50	91.1	2.28×10^3 (4.45×10^3)
13	**7**	–	0.25	26.3	6.58×10^2 (2.63×10^3)
14		TEMPO (2.5)	0.50	83.8	2.10×10^3 (4.19×10^3)
15	**8**	–	0.25	18.2	4.55×10^2 (1.82×10^3)
16		TEMPO (2.5)	0.50	66.8	1.67×10^3 (3.34×10^3)
17	**9**	–	0.25	13.8	3.46×10^2 (1.38×10^3)
18		TEMPO (2.5)	0.50	47.4	1.19×10^3 (2.37×10^3)
19	**10**	–	0.25	17.4	4.36×10^2 (1.74×10^3)
20		TEMPO (2.5)	0.50	59.2	1.48×10^3 (2.96×10^3)

[a]Reaction conditions unless stated otherwise: 5 mmol of substrate, 2 μmol (0.04 mol % vs substrate) of **1−10**, 10 mmol of TBHP (2 equiv, 70% in H_2O), 80 °C, 15−60 min reaction time, MW irradiation (10 W power). [b]Moles of acetophenone per 100 mol of 1-phenylethanol. [c]Turnover number = number of moles of product per mol of catalyst precursor; TOF = TON per hour (values in brackets).

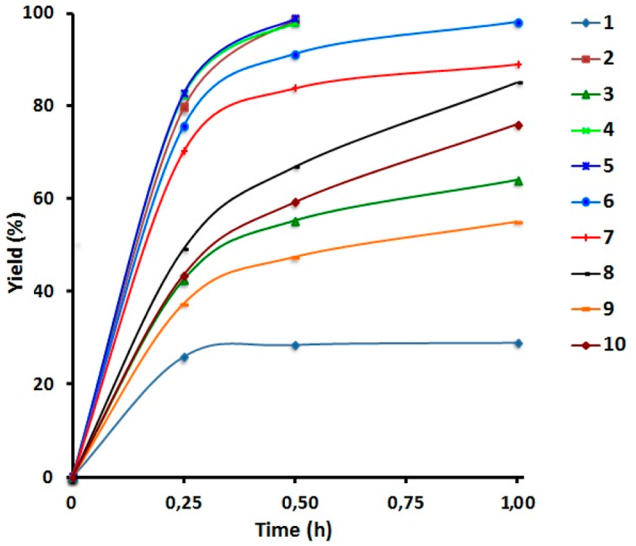

Figure 4. Effect of the reaction time on the yield for the MW-assisted and TEMPO-mediated solvent-free peroxidative oxidation of 1-phenylethanol to acetophenone catalyzed by **1−10**.

the coordination sphere of Cu^{II} appears to enhance the catalytic activity (compare e.g., **1** with **2** or **6**; Table 1, entries 2, 4 and 12, respectively). Blank tests (in the absence of the metal catalyst but in the presence of 2.5% TEMPO) led to the maximum acetophenone yield of 4.7%.

The MW-assisted reaction proceeds rapidly under the low irradiation power of 10 W (increasing the power up to 100 W did not show a significant yield enhancement) and is highly effective even in the presence of the very low amounts of catalyst (0.04 mol % vs substrate) used.

The oxidation of 1-phenylethanol by the **2** or **6**/TBHP/TEMPO/MW systems affords acetophenone in yields similar to those obtained by a copper complex with Schiff base and diethanolamine ligands[19d] or by alkoxy-1,3,5-triazapentadienato copper(II) complexes,[20e,l] but in much higher yields than in the presence of various mononuclear Cu(II) complexes bearing azathia macrocycles[20o,p] or dinuclear Mn(II) compounds.[20f,g] Similar yields are also observed with bi- or tetranuclear cage-like Cu(II) silsesquioxanes,[20m,n] although requiring much longer (4 and 2 h, respectively) reaction times, since conventional heating is used.

The MW-assisted oxidation of 1-phenylethanol with TBHP is believed to proceed mainly via a radical mechanism, as proposed for other copper complexes,[19,20] which involves both carbon- and oxygen-centered radicals.[24] The addition to the reaction mixture of Ph_2NH or $CBrCl_3$ (10 mmol) strongly hampers the catalytic activity. This suggests the generation of oxygen and carbon radicals in the reaction, which are trapped by those radical scavengers. The mechanism may involve free-radicals, e.g. $tBuO^{\bullet}$[20m,25] produced in the Cu (or Co)-promoted decomposition of TBHP. It may proceed via the coordination of 1-phenylethanol to an active site of the catalyst, and its deprotonation to form the ethoxide ligand, followed by a metal-centered (and TEMPO-assisted) dehydrogenation.[20b,26]

CONCLUSIONS

In the current work we explored novel cooperative metal and ligand effects in synthesis. In particular, easy one-pot template syntheses of new coordination compounds of varying nuclearities (Scheme 2) which also involve a remarkable auxiliary ligand-assisted *E*/*Z* isomerization of the AAMN ligands (Scheme 3) and an unprecedented simultaneous C≡N bond activation in 2-cyanopyridine and substituted malononitrile (Scheme 4) are reported. The proposed preparative methods allowed achieving an easy resolution of *E* and *Z* isomers that is of significance for synthetic and material chemistries.[16,18]

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The obtained complexes act as effective catalyst precursors for the mild and selective peroxidative oxidation of 1-phenylethanol to acetophenone in a solvent-free MW-assisted process; the mediation by TEMPO affords almost quantitative yields of the ketone. Reactions are fast, selective, require very small amounts of catalyst precursors and low power MW irradiation, and avoid the use of any added solvent, features of significance toward the development of benign environmental and energy-saving catalytic processes for such a type of reaction.

EXPERIMENTAL SECTION

Materials and Instrumentation. All the synthetic work was performed in air and at room temperature. All the chemicals were obtained from commercial sources (Aldrich) and used as received. Infrared spectra (4000−400 cm^{-1}) were recorded on a Vertex 70 (Bruker) instrument in KBr pellets. 1D (^1H, $^{13}C\{^1H\}$) NMR spectra were recorded on Bruker Avance II 300.13 (75.468 carbon-13) and 400.13 (100.61 carbon-13) MHz (UltraShield Magnet) spectrometers at ambient temperature. C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Electrospray mass spectra (ESI-MS) were run with an ion-trap instrument (Varian 500-MS LC Ion Trap Mass Spectrometer) equipped with an electrospray ion source. For electrospray ionization, the drying gas and flow rate were optimized according to the particular sample with 35 p.s.i. nebulizer pressure. Scanning was performed from m/z 100 to 1200 in methanol solution. The compounds were observed in the positive mode (capillary voltage = 80−105 V). The catalytic tests under MW irradiation were performed in a focused microwave Anton Paar Monowave 300 reactor (10 W), using a 10 mL capacity reaction tube with a 13 mm internal diameter, fitted with a rotational system and an IR temperature detector. Gas chromatographic (GC) measurements were carried out using a FISONS Instruments GC 8000 series gas chromatograph with a DB-624 (J&W) capillary column (FID detector) and the Jasco-Borwin v.1.50 software. The temperature of injection was 240 °C. The initial temperature was maintained at 120 °C for 1 min, then raised 10 °C/min to 200 °C, and held at this temperature for 1 min. Helium was used as the carrier gas. GC−MS analyses were performed using a PerkinElmer Clarus 600 C instrument (He as the carrier gas). The ionization voltage was 70 eV. Gas chromatography was conducted in the temperature-programming mode, using a SGE BPX5 column (30 m × 0.25 mm × 0.25 μm). Reaction products were identified by comparison of their retention times with known reference compounds, and by comparing their mass spectra to fragmentation patterns obtained from the NIST spectral library stored in the computer software of the mass spectrometer.

Preparation of Ligands. The syntheses and characterization of $NaHL^1$,[12c] H_2L^2,[12a] and $NaHL^3$[18a] were reported earlier and will not be discussed here.

For the synthesis of H_2L^4, 2-aminobenzoic acid (2.74 g, 20 mmol) was dissolved in 50 mL water, and 0.80 g (20 mmol) of NaOH was added. The solution was cooled in an ice bath to 273 K, and 1.38 g (20 mmol) of $NaNO_2$ was added; 4.00 mL HCl was then added in 0.5 mL portions for 1 h. The temperature of the mixture should not exceed 278 K. Methyl 2-cyanoacetate (2 mL, 20 mmol) was added to 30 mL water−ethanol (5/25, v/v) solution of sodium hydroxide (0.4 g, 10 mmol) and sodium acetate (1.64 g, 20 mmol). The resulting solution was stirred and cooled to ∼273 K, and a suspension of diazonium salt (see above) was added in three portions under vigorous stirring for 1 h. A yellow precipitate of the title compound was formed in ∼1 h, filtered off, dried in air, and recrystallized from methanol.

H_2L^4. Yield: 760 mg, 76% (based on methyl 2-cyanoacetate), yellow powder soluble in water, methanol, ethanol and acetone and insoluble in chloroform. Anal. Calcd for $C_{11}H_9N_3O_4$ (Mr = 247.21): C, 53.44; H, 3.67; N, 17.00; found: C, 53.38; H, 3.51; N, 16.79%. ESI-MS: m/z: 248.2 $[Mr + H]^+$. IR (KBr): 3475 and 3134 ν(OH), 2962 and 2885 ν(NH), 2238 and 2210 ν(C≡N), 1747 ν(COOH), 1710 and 1669 ν(C═O), 1606 and 1589 ν(C═N) cm^{-1}. ^1H NMR of a mixture of isomeric E- and Z-hydrazone forms (300.130 MHz) in DMSO-d_6, internal TMS, δ (ppm): E-Hydrazone, 3.86 (s, 3H, OCH_3), 7.26−7.99 (4H, Ar−H), 13.10 (s, 1H, N−H), 13.89 (s, 1H, O−H). Z-Hydrazone, 3.86 (s, 3H, OCH_3), 7.26−7.99 (4H, Ar−H), 13.97 (s, 1H, O−H), 14.59 (s, 1H, N−H). $^{13}C\{^1H\}$ NMR (75.468 MHz, DMSO-d_6). E-Hydrazone, δ: 52.90 (OCH_3), 107.69 (Ar−H), 114.94 (C≡N), 115.74 (2Ar−H), 123.99 (Ar−H), 131.36 (C═N), 134.93 (Ar−NHN═), 142.95 (Ar−COOH), 160.56 (C═O), 169.42 (COOH). Z-Hydrazone, δ: 52.90 (OCH_3), 106.90 (Ar−H), 110.71 (C═N), 115.12 (C≡N), 115.86 (2Ar−H), 124.48 (Ar−H), 134.68 (Ar−NHN═), 142.59 (Ar−COOH), 160.08 (C═O), 168.06 (COOH).

Syntheses of Complexes. *Synthesis of* ***1***. $NaHL^1$ (0.272 g, 1.0 mmol) was dissolved in 30 mL methanol, then 0.233 g (1.0 mmol) of $Cu(NO_3)_2{\cdot}2.5H_2O$ was added. The mixture was stirred under solvent reflux for 5 min, then 0.14 mL of $N(C_2H_5)_3$ was added, and the system stirred 30 min and left for slow evaporation. Black crystals of the product started to form after ∼4 d at room temperature; they were then filtered off and dried in air.

1: Yield, 39 mg, 61% (based on Cu). Black crystals soluble in ethanol, acetonitrile, DMSO, and water. Anal. Calcd for $C_{10}H_{14}CuN_4O_7S$ (Mr = 397.85): C, 30.19; H, 3.55; N, 14.08. Found: C, 29.51 H, 3.26; N, 13.33. ESI-MS: m/z: 381.1 $[Mr - H_2O + H]^+$. IR (KBr, selected bands, cm^{-1}): 3298 ν(O−H), 2950 ν(N−H), 2212 ν(C≡N), 1657 and 1613 ν(C═N).

Syntheses of ***2*** *and* ***3***. $NaHL^1$ (0.272 g, 1.0 mmol) was dissolved in 15 mL water−acetone mixture (1/3, v/v), then 0.233 g (1.0 mmol) of $Cu(NO_3)_2{\cdot}2.5H_2O$ and 0.121 g (1.0 mmol) 1-(pyridin-3-yl)ethanone (1-(pyridin-4-yl)ethanone in the case of **3**) were added. The mixture was stirred and heated to 80 °C for 5 min, then 0.14 mL of $N(C_2H_5)_3$ was added, stirred 30 min at 80 °C, and left for slow evaporation. Green crystals of the product started to form after ∼3 d at room temperature; they were then filtered off and dried in air.

2: Yield, 35 mg, 55% (based on Cu). Dark-green crystalline compound soluble in ethanol, methanol, acetonitrile, and water. Anal. Calcd for $C_{16}H_{17}CuN_5O_7S$ (Mr = 486.95): C, 39.46; H, 3.52; N, 14.38. Found: C, 40.14; H, 3.39; N, 14.27. ESI-MS: m/z: 469.2 $[Mr - H_2O + H]^+$. IR (KBr, selected bands, cm^{-1}): 3590 and 3487 ν(O−H), 3375, 3316, 3235, 3081, and 3012 ν(N−H), 2202 ν(C≡N), 1686 and 1646 ν(C═O), 1564 ν(C═N).

3: Yield, 34 mg, 53% (based on Cu). Dark-green crystalline compound soluble in ethanol, methanol, acetonitrile, and water. Anal. Calcd for $C_{16}H_{13}CuN_5O_5S$ (Mr = 450.92): C, 42.62; H, 2.91; N, 15.53. Found: C, 42.53; H, 2.83; N, 15.39. ESI-MS: m/z: 451.8 $[Mr + H]^+$. IR (KBr, selected bands, cm^{-1}): 3414, 3322, 3246, and 3195 ν(N−H), 2203 ν(C≡N), 1694 and 1649 ν(C═O), 1561 ν(C═N).

Synthesis of ***4***. Addition, under stirring, of $N(C_2H_5)_3$ (0.14 mL) to a solution of H_2L^2 (0.214 g, 1.0 mmol) and $Co(NO_3)_2{\cdot}6H_2O$ (0.291 g, 1.0 mmol) in 30 mL of methanol, followed by stirring for 30 min at 80 °C, gave a brown precipitate when the reaction mixture was left cooling down to room temperature. It was collected by filtration, washed with cold methanol, and dried under vacuum. The crystals of **4** suitable for X-ray structural analysis were obtained by slow evaporation of a mixture of acetone/DMF (6:1) solution of the precipitated brown solid.

4: Yield, 42 mg, 66% (based on Co). Brown crystals soluble in ethanol, acetonitrile, DMSO, and DMF. Anal. Calcd for $C_{34}H_{48}Co_2N_{12}O_{12}$ (Mr = 934.68): C, 43.69; H, 5.18; N, 17.98. Found: C, 43.72 H, 5.23; N, 17.89. ESI-MS: m/z: 789.5 $[Mr - 2(CH_3)_2NCHO + H]^+$. IR (KBr, selected bands, cm^{-1}): 3471 ν(O−H), 3307 ν(N−H), 2209 ν(C≡N), 1636 ν(C═O), 1580 and 1551 ν(C═N).

Syntheses of ***5*** *and* ***6***. $NaHL^3$ (0.305 g, 1.0 mmol) was dissolved in 15 mL methanol, then 0.233 g (1.0 mmol) of $Cu(NO_3)_2{\cdot}2.5H_2O$ and 0.122 g (1.0 mmol) *syn*-2-pyridinealdoxime (0.10 mL, pyridine in the case of **6**) were added. The mixture was stirred for 30 min at 80 °C and left for slow evaporation; the green crystals of the product started to form after ∼3 d at room temperature; they were then filtered off and dried in air.

5: Yield, 38 mg, 59% (based on Cu). Light-green crystalline compound soluble in ethanol, methanol, acetonitrile, and water. Anal.

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Calcd for $C_{29}H_{28}Cu_3N_{10}O_{13}S$ (*Mr* = 947.29): C, 36.77; H, 2.98; N, 14.79. Found: C, 36.53; H, 2.85; N, 14.48. ESI-MS: *m*/*z*: 853.2 [*Mr* − NO_3 − CH_3OH]$^+$. IR (KBr, selected bands, cm^{-1}): 3345 ν(O−H), 2967 ν(N−H), 2218 ν(C≡N), 1705 ν(C═O), 1586 ν(C═N).

6: Yield, 43 mg, 67% (based on Cu). Dark-green crystalline compound soluble in ethanol, methanol, acetonitrile, and water. Anal. Calcd for $C_{15}H_{14}CuN_4O_6S$ (*Mr* = 441.91): C, 40.77; H, 3.19; N, 12.68. Found: C, 40.36; H, 3.02; N, 12.73. ESI-MS: *m*/*z*: 442.8 [*Mr* + H]$^+$. IR (KBr, selected bands, cm^{-1}): 3437 ν(O−H), 2220 ν(C≡N), 1656 ν(C═O), 1589 ν(C═N).

Synthesis of ***7***. H_2L^4 (0.234 g 1.0 mmol) was dissolved in 15 mL methanol, then 0.233 g (1.0 mmol) of $Cu(NO_3)_2{\cdot}2.5H_2O$ and 0.14 mL $N(C_2H_5)_3$ were added. The mixture was stirred and heated to 80 °C for 30 min and then left at room temperature for slow evaporation; deep-green crystals of **7** suitable for X-rays started to form after ∼5 d.

7: Yield, 41 mg, 64% (based on Cu). Dark-green crystalline compound soluble in ethanol, methanol, acetonitrile, and water. Anal. Calcd for $C_{11}H_{13}CuN_3O_7$ (*Mr* = 362.78): C, 36.42; H, 3.61; N, 11.58. Found: C, 36.25; H, 3.39; N, 11.42. ESI-MS: *m*/*z*: 345.7 [*Mr* − H_2O + H]$^+$. IR (KBr, selected bands, cm^{-1}): 3338, 3162, and 2958 ν(O−H), 2219 ν(C≡N), 1709 ν(C═O), 1582 ν(C═N).

Syntheses of ***8*****−*****10***. $NaHL^1$ (0.272 g 1.0 mmol) was dissolved in 15 mL water−acetone mixture (1/3, v/v) (methanol in the case of **9** and **10**), then 0.233 g (1.0 mmol) of $Cu(NO_3)_2{\cdot}2.5H_2O$ and 0.104 g (1.0 mmol) 2-cyanopyridine (4-cyanopyridine in the case of **10**) were added (also 0.14 mL of $N(C_2H_5)_3$ was also added in the case of **9** and **10**). The mixture was stirred and heated to 80 °C for 30 min and left for slow evaporation. The bulky light-greenish (green in the case of **9** and **10**) crystals of the product started to form after ∼4 d at room temperature; they were then filtered off and dried in air.

8: Yield, 40 mg, 63% (based on Cu). Light-green crystalline compound soluble in ethanol, methanol, acetonitrile- and water. Anal. Calcd for $C_{30}H_{30}CuN_{12}O_{12}S_2$ (*Mr* = 878.32): C, 41.02; H, 3.44; N, 19.14. Found: C, 41.12; H, 3.31; N, 18.89. ESI-MS: *m*/*z*: 844.3 [*Mr* − $2H_2O$ + H]$^+$. IR (KBr, selected bands, cm^{-1}): 3349 and 3201 ν(O−H), 2788 and 2744 ν(N−H), 2227 ν(C≡N), 1674 ν(C═O), 1576 ν(C═N).

9: Yield, 39 mg, 61% (based on Cu). Green crystalline compound soluble in ethanol, methanol, acetonitrile- and water. Anal. Calcd for $C_{17}H_{20}CuN_6O_7S$ (*Mr* = 515.99): C, 39.57; H, 3.91; N, 16.29. Found: C, 39.43; H, 3.86; N, 16.10. ESI-MS: *m*/*z*: 480.9 [*Mr* − $2H_2O$ + H]$^+$. IR (KBr, selected bands, cm^{-1}): 3436 and 3241 ν(O−H), 3103, 3074, 2992, and 2947 ν(N−H), 2216 ν(C≡N), 1674, 1619, and 1596 ν(C═N).

10: Yield, 40 mg, 62% (based on Cu). Green crystalline compound soluble in ethanol, methanol, acetonitrile, and water. Anal. Calcd for $C_{16}H_{14}CuN_6O_5S$ (*Mr* = 465.93): C, 41.24; H, 3.03; N, 18.04. Found: C, 41.05; H, 3.00; N, 18.12. ESI-MS: *m*/*z*: 466.9 [*Mr* + H]$^+$. IR (KBr, selected bands, cm^{-1}): 3455 ν(O−H), 2944 and 2677 ν(N−H), 2213 ν(C≡N), 1614 ν(C═N).

X-ray Structure Determinations. Independent reflection data for **1**−**10** were collected with Mo Kα at 150 K (293 K for **2** and **3**) using the Oxford Diffraction X-Calibur CCD System. The crystals were positioned at 50 mm from the CCD, and 321 frames were measured with counting times of 10 s. Data analyses were carried out with the CrysAlis program.[27a] The structures were solved using direct methods with the SHELXS97 program[27b] and refined on F^2 with the SHELXL97 program.[27b] The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Some hydrogen atoms on solvent water molecules could not be located. When they were located they were refined with distance constraints. Absorption corrections were carried out using the ABSPACK program.[27c] Details of the structures have been deposited at the Cambridge Crystallographic Data Centre as CCDC 998495−998504. CCDC 998495−998504 contain the supplementary crystallographic data for complexes **1**−**10**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

General Procedure for the Peroxidative Oxidation of 1-Phenylethanol. In a typical experiment, 1-phenylethanol (5.00 mmol), TBHP (70% aqueous solution, 10.0 mmol) and catalyst precursor **1**−**10** (2 μmol, 0.04 mol % vs substrate) were introduced to a cylindrical Pyrex tube, which was then placed in the focused microwave reactor. In the TEMPO-mediated experiments, TEMPO (125 μmol) was added to the reaction mixture. The system was stirred and irradiated (10 W) for 15 min at 80 °C. After the reaction, the mixture was allowed to cool down to room temperature. Benzaldehyde, 300 μL, (internal standard) and 5 mL of NCMe (to extract the substrate and the organic products from the reaction mixture) were added. The obtained mixture was stirred during 10 min, and then a sample (1 μL) was taken from the organic phase and analyzed by GC (or GC−MS) using the internal standard method. Blank tests indicate that only traces (<1.9%) of acetophenone are generated in a Cu-free system.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

$^1H/^{13}C$ NMR spectrum of H_2L^4. Crystal data, experimental parameters, and selected details of the refinement calculations, tables listing bond distances and angles and hydrogen bond geometry of compounds **1**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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