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Water-Soluble Cobalt(II) and Copper(II) Complexes of 3-(5-Chloro-2-hydroxy-3-sulfophenylhydrazo)pentane-2,4-dione as Building Blocks for 3D Supramolecular Networks and Catalysts for TEMPO-Mediated Aerobic Oxidation of Benzylic Alcohols

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A new water-soluble β-diketone azo derivative – 3-(5-chloro-2-hydroxy-3-sulfophenylhydrazo)pentane-2,4-dione (H_3L, **1**) – was synthesized and found to be stable in DMSO solution and in the solid state in the hydrazo tautomeric form. Its water-soluble complexes $[Co(HL)(en)(H_2O)]\cdot 4H_2O$ (**3**) and the zwitterionic $[Cu(L)(Hen)(H_2O)]$ (**4**), with buffering properties, were prepared by reaction of cobalt(II) and copper(II) nitrates with the ethylenediammonium (H_2en) salt of **1**, $(H_2en)(HL)$ (**2**). In the formation of **3** and **4**, **1** is a chelating ligand, and a crucial synthetic and structural role is played by en, allowing the organization of water-soluble assemblies and influencing the overall 3D supramolecular arrangement. Compound **3** is the first cobalt complex with an azo derivative of a β-diketone. Complex **4** acts as catalyst precursor for the aerobic TEMPO-mediated selective oxidation of benzylic alcohols to the corresponding aldehydes in aqueous media.

Introduction

Catalytic processes in aqueous media can require constrained active particles in the water phase, and the design of homogeneous water-soluble catalysts usually involves the use of a suitable ligand with a hydrophilic functionality.[1] In most cases such a ligand can be obtained by attaching a water-solubilizing group, e.g. a sulfonato or carboxylato group. Another major challenge is the reversible tuning of the acid–base properties of the catalyst, which can enhance the activity/selectivity towards a certain product and/or reversibly change the hydrophilicity. In addition, since many processes require a certain pH interval, a complex that, apart from its main catalytic function, can maintain the pH within a certain range (i.e. possessing buffer properties) is needed. Thus, the synthesis of water-soluble complexes with several pH-tunable sites for protonation–deprotonation is of interest for new green catalytic processes.

One potentially interesting process is the selective oxidation of alcohols by dioxygen or air[2] using a combination of TEMPO radicals (2,2,6,6-tetramethylpiperidine-1-oxyl), or its derivatives, with copper complexes.[3] Our preliminary studies[4] have shown that copper(II) complexes with functionalized azo derivatives of β-diketones (ADBs), in particular *ortho*-hydroxy-substituted ADBs, are significantly active in the aerobic oxidation of benzyl alcohols to aldehydes. Hence, we report our continued preparation of new water-soluble ADB copper(II) and cobalt(II) complexes, which contain sites for possible pH regulation properties, in particular sulfo and amino groups, considered to be good candidates to fulfil these goals.

From another perspective, ADBs and their complexes can create interesting supramolecular architectures involving monomeric, oligomeric or polymeric subunits.[4,5] Ethylenediamine (en) can further participate in this process through template Schiff base condensation or as a proton-rich attractor and spacer, allowing the regulation of the size of channels or cavities within the H-bonded assemblies.[6] In addition, the presence of proton acceptor and donor sites within one molecule will result in a pH-tunable arrangement (association), which is interesting for a wide range of applications.[7] Hence, the complexes created with these types of ligands can be used as promising new building blocks in various multicomponent supramolecular architectures.

Therefore, based on these considerations, this work has been undertaken with the following aims: i) to synthesize new water-soluble cobalt(II) and copper(II) complexes with 3-(5-chloro-2-hydroxy-3-sulfophenylhydrazo)pentane-2,4-dione (**1**, H_3L), ii) to explore their potential as building blocks in supramolecular hydrogen-bonded assemblies, and iii) to

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apply these complexes as catalysts for the aerobic TEMPO-mediated selective oxidation of benzylic alcohols to the corresponding aldehydes.

Results and Discussion

Synthesis, Spectroscopic and Crystallographic Investigation of 1–4

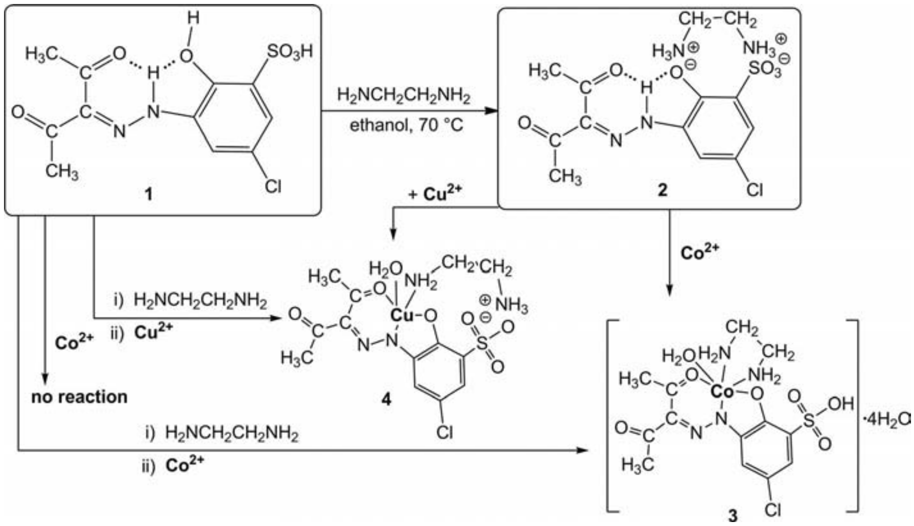
The new water-soluble ligand **1** (see Scheme S1, Supporting Information) was synthesized by a modified method[8a–8c] by reacting 5-chloro-2-hydroxy-3-sulfophenyldiazonium chloride and pentane-2,4-dione in a water solution containing sodium hydroxide.[8d] 5-Chloro-2-hydroxy-3-sulfophenyldiazonium chloride was obtained by diazotization of the substituted aniline. Compound **1** is highly soluble in polar solvents such as water, DMF, and DMSO, but almost insoluble in chloroform, dichloromethane, and toluene. The presence of the SO_3H group is crucial for water solubility; the analogue of **1** with H instead of this group is completely insoluble in water.[9]

The NMR spectrum of **1** in [D$_6$]DMSO at room temperature indicates that this compound exists in this solvent in the hydrazo rather than in the enol-azo or keto-azo form (Scheme S2, Supporting Information). The two peaks of the acetyl groups in the ^{1}H and ^{13}C NMR spectra (see Experimental Section) indicate that one of these groups undergoes a shift due to hydrogen bonding of the carbonyl moiety with the hydrazo NH group. This is in agreement with the low field chemical shift (δ =14.33 ppm) of the hydrazo NH proton and is also consistent with IR data: the stretching bands ν(C=O) and ν(C=O···H) are at 1677 and 1624 cm^{-1}, respectively, the latter being shifted on account of the H-bond.[4,5] The ν(OH) and ν(NH) bands at 3400 and 3094 cm^{-1} also support the existence of the H-bonded hydrazone structure in the solid state.[4,5] X-ray diffraction analyses of analogues of **1**, with different substituents, demonstrate that they are stabilized in the hydrazo II rather than in the hydrazo I form.[4]

It has been demonstrated[10] that in solution cobalt(II) ions interact with **1**, but attempts to prepare complexes in the solid state by concentration of solutions of cobalt(II) nitrate and **1** failed (this strategy was used for the preparation of some copper(II)–ADB complexes).[4] In fact, evaporation of methanol, ethanol, DMF, water, and DMSO (or their mixtures) solutions of cobalt salts with **1** gave only mixtures of the starting materials, whereas, in the case of copper(II) salts, amorphous powders of unidentified product mixtures were obtained. To solve this problem, **1** was deprotonated by addition of en and the salt (H_2en)(HL) (**2**) was used as the starting material for further reactions with Co^{II} and Cu^{II} nitrate salts to afford [Co(HL)(en)(H_2O)]·4H_2O (**3**) (the first Co–ADB complex to be reported) and [Cu(L)(Hen)(H_2O)] (**4**), respectively (Scheme 1). The added en conceivably weakens the hydrogen-bonded system in **1** (see below) and the reactivity of activated **1** increases, facilitating the N–H deprotonation and coordination to the metal ion.

Alternatively, **3** and **4** can be prepared by **2** formed in situ, upon neutralization of **1** with en in solution and subsequent addition of the cobalt(II) or the copper(II) salt. In any case, the complex product can be isolated in the solid state upon concentration of the reaction solution left to evaporate slowly. Interestingly, the interaction of en with **1** does not provide a Schiff base, which is in contrast to its reaction with β-diketones[11] and other ADBs,[4] possibly due to electrostatic repulsion.

The ^{1}H NMR spectrum of **2**, compared with that of **1**, shows the shift of the hydrazo NH proton from δ = 14.33 to 15.20 ppm and the absence of the *ortho*-OH proton of **1** (δ = 11.23 ppm), whereas in the ^{13}C NMR spectrum the H-bonded carbonyl group is shifted from δ = 196.5 to 172.4 ppm. To study the structural features of **2** and find out which tautomeric form is stabilized in the solid state after deprotonation with en, single crystals of **2** were prepared by slow evaporation of its ethanol solution at room temperature. Compound **2** crystallizes in the triclinic space



Scheme 1. Synthesis of **2**–**4**.

group $P\bar{1}$ with almost planar overall geometry of the anion (Table S1 and S2). In accord with previous findings,[12] the molecular structure of the anionic part of **2** contains an intramolecular six-membered hydrogen-bonded ring with a strong hydrogen bond (Figure 1), as suggested by the geometric parameters (Table S3). This behavior is well described by the intramolecular resonance assisted hydrogen bond model, which relates to the synergistic mutual reinforcement of intramolecular hydrogen bonding due to π-electron delocalization.[12a,12c,13] The geometry, the typical double bond length of C(7)–N(2) [1.345(2) Å] (Table S2, Figure 1), and the formation of the intramolecular N–H···O hydrogen bond indicate that the hydrazone is the preferred tautomeric form of the molecule.[4] However, the N(1)–N(2) distance (1.290 Å) suggests a partial double bond character for this bond and thus some degree of conjugation with the aromatic ring.

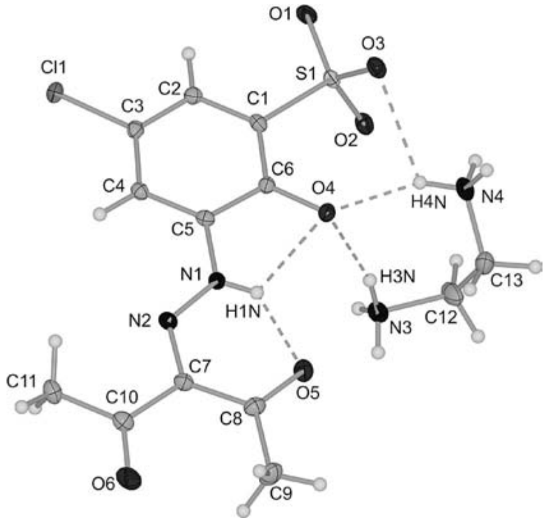


Figure 1. Structure of **2** (ellipsoids are drawn at 50% probability). Selected bond lengths [Å] and angles [°]: O(4)–C(6) 1.316(2), O(5)–C(8) 1.241(2), O(6)–C(10) 1.229(2), N(2)–C(7) 1.345(2), N(1)–H(1N) 0.8115, H(1N)···O(4) 2.23, H(1N)···O(5) 1.89, N(1)–H(1N)···O(4) 2.634(5), N(1)–H(1N)···O(5) 2.529(4), N(4)–H(4N)···S(1) 3.5448(18), N(1)–H(1N)–O(4) 111.09, N(1)–H(1N)–O(5) 135.28.

The cobalt atom in **3** is six-coordinate (Figure 2, a). The Co–O bond lengths range from 1.862(3) to 1.958(3) Å, whereas the Co–N distances are within 1.857(3)–1.967(3) Å (Table S2). The coordination environment of the cobalt is best described as distorted octahedral (4 + 2) with en (N3) and a water molecule (O7) coordinated in the axial positions. The cobalt atom belongs to (i) two fused five- and six-membered metallacycles, Co1–O4–C6–C5–N6 and Co1–O5–C8–C7–N5–N6 and (ii) the five-membered metallacycle Co1–N3–C12–C13–N4 (in this case both N atoms of en are coordinated to cobalt, in contrast to **4**). The sixth coordination position is occupied by H_2O. This coordinated water molecule and one part of en are *anti* to each other and involved in two hydrogen bonds with the noncoordinated water molecules. The average H_2O···O, H_2O···Cl, H_2O···S, and H_2O···N distances of the hydrogen bonds in **3** fall within the 2.655(4)–3.629(4) Å range (Table S3), consistent with strong hydrogen bonding.[12,13] Thus, **3** is combined in a 3D network with channels (Figure 2, b), in which water molecules interconnect carbonyl oxygen atoms, oxygen atoms of the anions, and other water molecules. In accord with the geometry of the complexes, the channels incorporating the coordinated water have a nearly quadratic cross section, whereas those containing hydrate water molecules have an elongated profile. There are abundant hydrogen bonds (Table S3) as well as π···π stacking interactions of 4.6228(4) Å which extend the 2D frameworks into a 3D supramolecular architecture (Figure 2, b). Moreover, building blocks of **3** are associated in layers separated by water molecules.

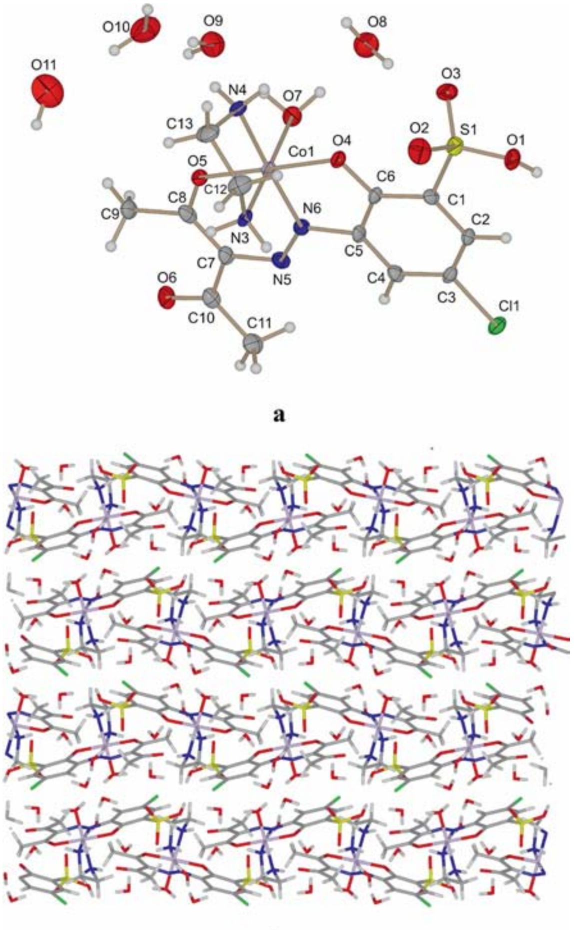


Figure 2. Structure of **3** (a) (ellipsoids are drawn at 50% probability) with packing diagram (b). Selected bond lengths [Å] and angles [°]: Co(1)–O(4) 1.874(3), Co(1)–O(5) 1.862(3), Co(1)–O(7) 1.958(3), Co(1)–N(3) 1.926(3), Co(1)–N(4) 1.967(3), Co(1)–N(6) 1.857(3), N(6)–Co(1)–O(5) 93.34(13), N(6)–Co(1)–O(4) 86.72(12), O(5)–Co(1)–O(4) 179.21(11), N(3)–Co(1)–O(7) 177.81(13), O(4)–Co(1)–N(4) 88.99(13).

X-ray structural analysis of **4** shows that it crystallizes as a zwitterionic neutral mononuclear complex in the triclinic space group $P\bar{1}$, with the ADB ligand, the coordinated water, and Hen in the asymmetric unit (Figure 3, a, Scheme 1). The coordination polyhedron of the Cu atom is tetragonal pyramidal with the O(3) atom in the axial position. ADB acts as a tridentate ligand by means of the deprotonated OH group in the *ortho* position (O1) of the aromatic part, of one of the nitrogen atoms (N1) of Hen, and one oxygen atom (O2) from a carbonyl group. The copper(II) atom belongs to two six- and five-membered fused metallacycles. The Cu(1)–O(1) bond length of 1.941(2) Å within the five-membered ring is shorter than that of the Cu(1)–O(2) bond [1.953(2) Å]. An extensive interlinkage of neighboring **4** molecules takes place through intermolecular H-bonds between the free carbonyl oxygen atom O7 and the protonated N4 atom of Hen, thus giving rise to supramolecular cationic chains (Figure 3, b). Hence, the protonated N4 atom of en acts as an H-donor bridging to O4, O5, O7, and S1 atoms of **4** in the neighboring unit (Table S3). On the other hand, intermolecular H-bonds between the coordinated water molecules and carbonyl oxygen atom O2 or the sulfo group oxygen atoms O5, O6 of two vicinal molecules lead to chains. Moreover, H-bonds are formed between the coordinated N3 atom of en and O(4)#4, O(6)#2, and S(1)#2. Additionally, intermolecular π···π interactions are observed between the C1–C6 phenyl ring and the Cu1–N1–N2–C7–C10–O2 metallacycle (*x* + 1, *y*, *z*); the centroid···centroid distance of 3.5280(1) Å and the angle between the planes, 6.73°, indicate a π···π interaction (Figure S1).

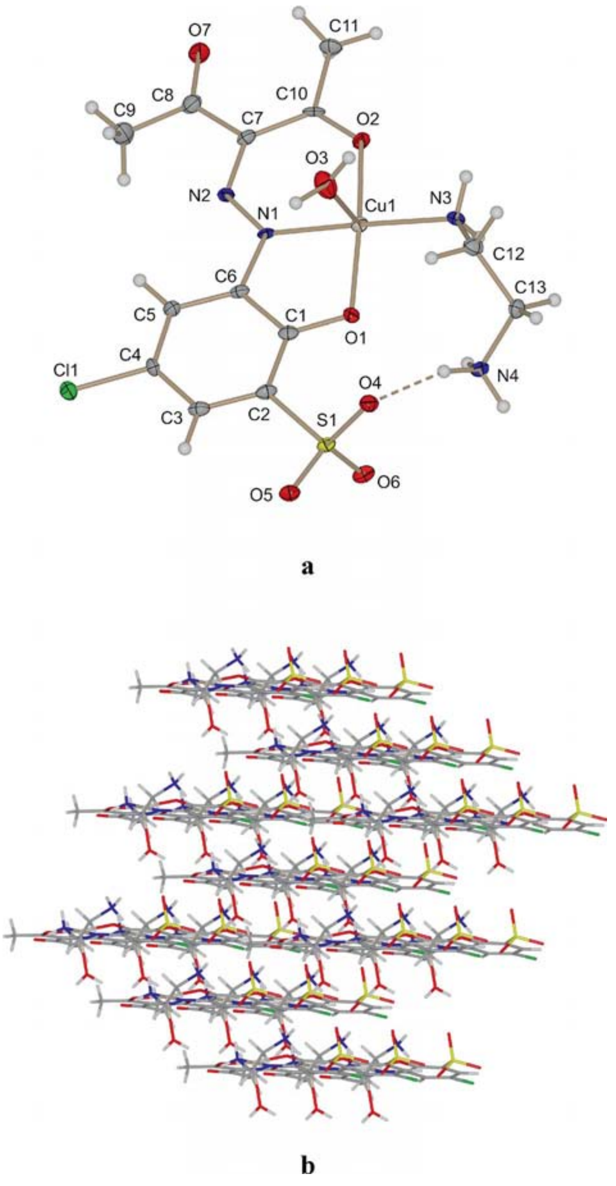


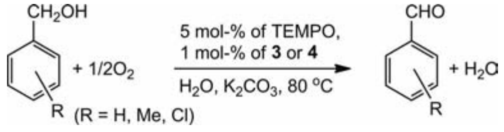
Figure 3. Structure of **4** (a) (ellipsoids are drawn at 50% probability) with packing diagram (b). Selected bond lengths [Å] and angles [°]: Cu(1)–N(1) 1.928(3), Cu(1)–O(1) 1.941(2), Cu(1)–O(2) 1.953(2), Cu(1)–N(3) 2.002(3), Cu(1)–O(3) 2.3521(19), N(1)–Cu(1)–O(1) 84.73(10), N(1)–Cu(1)–O(2) 89.09(9), N(1)–Cu(1)–O(3) 87.63(8), N(3)–Cu(1)–O(3) 91.83(9), O(1)–Cu(1)–O(3) 89.40(8), O(1)–Cu(1)–N(3) 93.02(9), O(2)–Cu(1)–O(3) 99.53(8), N(4)–H(4NA)···O(5)#4 2.852(3), N(4)–H(4NA)···O(4)#4 3.160(3), N(4)–H(4NB)···O(4) 2.842(3), N(4)–H(4NA)···S(1)#4 3.582(2). Symmetry transformations used to generate equivalent atoms: #4 *x* – 1, *y*, *z*.

Buffer Properties of 4

The zwitterionic nature of **4** can be used in applications where pH-tunable or buffer properties of the system are crucial for the optimal performance of a specific function (e.g. in catalysis). An important characteristic of a zwitterionic compound is its isoelectric point, which was determined as 4.96 for **4** (see Supporting Information for details, Tables S4, S5), and its buffer zones lie in the weak acidic region with pH close to pK_2 = 6.84 (where K_2 is the deprotonation constant of **4** concerning the H_3N^+ group of Hen) and in the acid area with pH close to pK_1 = 3.08 (where K_1 concerns the deprotonation of the SO_3H group). Interestingly, possibly due to the formation of the zwitterion, the detection limit for the analytical determination of copper(II) with **2** (in the formation of **4**) decreases in comparison to **1** and other similar reagents,[14] therefore, both the sensitivity and selectivity are enhanced (Tables S6, S7).

Catalytic Activity of 3 and 4

Copper(II) complexes with N,N- and N,O-donor ligands have been found to be efficient catalysts for the TEMPO-mediated aerobic oxidation of benzylic alcohols in basic aqueous media (Scheme 2).[4,15] The catalysts lead to more efficient oxidation by promoting deprotonation of the alcohol.[15] Thus, we have applied **4** and, for comparison, **3** to check their potential as catalysts for this reaction in previously optimized reaction conditions.[4]



Scheme 2. Oxidation of benzyl alcohols using **3** and **4** as catalyst precursors.

Aerobic oxidation of benzyl alcohol (1.5 mmol) in aqueous alkaline (0.1 M K_2CO_3) solution, in the presence of a catalytic amount of **4** and TEMPO, gave benzaldehyde in

Table 1. Aerobic oxidation of selected alcohols to the corresponding aldehydes.[a].

Run	Complex	Substrate	Product	Time [h]	Yield [%][b]	TON/TOF [h^{-1}][c]
1	**4**	benzyl alcohol	benzaldehyde	6	68	68/11
2	**4**	benzyl alcohol	benzaldehyde	18	98	98/5.4
3	**3**	benzyl alcohol	benzaldehyde	6	< 1	1/0.2
4	**3**	benzyl alcohol	benzaldehyde	22	4	4/0.2
5[d]	**4**	benzyl alcohol	benzaldehyde	22	3	3/0.1
6[e]	**4**	benzyl alcohol	benzaldehyde	22	2	2/0.1
7	**4**	2-Me-benzyl alcohol	2-Me-benzaldehyde	18	74	74/4.1
8	**4**	3-Me-benzyl alcohol	3-Me-benzaldehyde	18	88	88/4.9
9	**4**	4-Me-benzyl alcohol	4-Me-benzaldehyde	18	97	97/5.4
10	**4**	4-Cl-benzyl alcohol	4-Cl-benzaldehyde	18	98	98/5.4
11	$Cu(NO_3)_2$	benzyl alcohol	benzaldehyde	6	20	20/3.3

[a] Conditions: 1.5 mmol of the substrate, 0.015 mmol (1 mol-%) of catalyst and 0.075 mmol (5 mol-%) of TEMPO in 5 mL of 0.1 M K_2CO_3 aqueous solution, 80 °C, 1 atm. air. [b] Yields based on GC analyses, selectivity in all cases $> 99\%$. [c] TON = mol of product/mol of catalyst; TOF = TON/h. [d] Reaction without K_2CO_3. [e] Reaction without TEMPO.

68% yield after 6 h (Table 1, run 1), and extension of the reaction time to 18 h significantly increased the yield (98%, run 3). The yields obtained with **3** were poor, even after 22 h (runs 3 and 4). In agreement with previously reported observations,[4,15] we also found that the presence of base (K_2CO_3) as well as TEMPO is crucial to obtain high yields (see runs 5–6, without these reagents).

Substituted benzylic alcohols can be also converted into the corresponding aldehydes in moderate to good yields. For example, oxidation of 2-, 3-, and 4-methylbenzyl alcohol results in 74, 88, and 97% yield of the corresponding aldehydes, respectively, revealing the steric effect of the methyl substituent position (runs 7–9). 4-Chlorobenzyl alcohol is also converted to 4-chlorobenzaldehyde in very good yield (98%, run 10). With $Cu(NO_3)_2$ instead of **3** or **4**, only 20% yield of benzaldehyde was achieved (run 11). We expect that these catalytic systems follow the previously proposed mechanism,[4,15,16] which involves coordination of RCH_2OH (or deprotonated RCH_2O^-) and the TEMPO radical to the copper(II) center, hydrogen abstraction from the α-carbon by TEMPO, and intramolecular electron transfer from the resulting *O*-ligated radical $RC^{\cdot}HO$ to Cu^{II} giving RCHO and Cu^{I}, which is subsequently reoxidized to Cu^{II}.

Conclusions

A new hydrazone compound **1** and its en salt **2** have been synthesized and shown to be stable in solution and in the solid state in the hydrazo form. The new pH-tunable water soluble zwitterionic Cu^{II} complex **4** and the first example of a Co^{II}–ADB complex **3** (Scheme 1) with labile H_2O ligands have been prepared and structurally characterized. Thus, **1** has proved to be a chelating ligand for complexation with Co^{II} and Cu^{II}. The complexes also bear ethylenediamine as a coligand, which plays a crucial structural role in the organization of the water-soluble assemblies influencing the overall 3D supramolecular arrangement, depending on the reaction conditions. These observations are of significance for the design of self-assembled coordination organic–inorganic materials[17] or smart functional materials attributed to tautomerism.[12a] For example, at given conditions, 3D supramolecular networks are formed by **3** and **4** through extensive intermolecular H-bonds. These features should be accounted for in further exploration of the rare intramolecular $NH_3^{+}\cdots{}^{-}O_3S$ interaction and H-bonding abilities of the ADB–en systems in crystal engineering in aqueous media.

Moreover, the water-soluble zwitterionic **4** has buffering properties and exhibits a good catalytic activity towards the aerobic TEMPO-mediated selective oxidation of benzylic alcohols to the corresponding aldehydes in aqueous basic medium, which could be extended to other H-bonded ADB systems and oxidation reactions, broadening their application in catalysis under green conditions, an underdeveloped field for supramolecular metal assemblies.

Experimental Section

Materials and Instrumentation: All chemicals were obtained from commercial sources and used as received. The ^1H and ^{13}C NMR spectra were recorded at ambient temperature with a Bruker Avance II + 300 (UltraShield™ Magnet) spectrometer operating at 300.130 and 75.468 MHz for ^1H and ^{13}C NMR, respectively. The chemical shifts are reported in ppm using tetramethylsilane as an internal reference. IR spectra (4000–400 cm^{-1}) were recorded with a BIO-RAD FTS 3000MX instrument as KBr pellets. Carbon, hydrogen, and nitrogen elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. All the synthetic work was performed in air and at room temperature. Chromatographic analyses were performed with 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.

Synthesis of H_3L (1): Compound **1** was synthesized according to the Japp–Klingemann reaction[8] from the corresponding diazonium salt and pentane-2,4-dione.

Diazotization: 5-Chloro-2-hydroxy-3-sulfoaniline (0.025 mol) was dissolved in water (50 mL) and crystalline NaOH (1.0 g) was added. The solution was cooled to 0 °C and $NaNO_2$ (0.025 mol) was added followed by 33% HCl (25 × 0.2 mL portions) over 1 h with vigorous stirring. During the reaction, the temperature of the mixture did not exceed +5 °C. A suspension of the unstable 5-chloro-2-hydroxy-3-sulfophenyldiazonium chloride was obtained

(Supporting Information, Scheme S1), which was used without purification for the next stage (see below).

Azocoupling: NaOH (0.025 mol) was added to a mixture of pentane-2,4-dione (0.025 mol) with water (50 mL). The solution was cooled in an ice bath, and a suspension of 5-chloro-2-hydroxy-3-sulfophenyldiazonium chloride (prepared as above) was added in two equal portions with vigorous stirring for 1 h. The following day, 3-(5-chloro-2-hydroxy-3-sulfophenylhydrazo)pentane-2,4-dione (H_3L, **1**) formed as a precipitate was collected by filtration, recrystallized from methanol, and dried in air; yield 77% (based on pentane-2,4-dione), dark brown powder, soluble in water, DMSO, ethanol, and dimethylformamide and insoluble in acetone and chloroform. $C_{11}H_{11}ClN_3O_6S$ (334.73): calcd. C 39.47, H 3.31, N 8.37; found C 39.35, H 3.27, N 8.30. IR (KBr): $\tilde{\nu}$ = 3400 [ν(OH)], 3094 [ν(NH)], 1677 [ν(C=O)], 1624 [ν(C=O···H)], 1588 [ν(C=N)], 732 [δ(CH, Ar)] cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 2.44 (s, 3 H, CH_3), 2.50 (s, 3 H, CH_3 signals overlapped with the solvent peak), 7.23–7.92 (2 H, Ar–H), 11.23 (s, 1 H, OH), 14.33 (s, 1 H, NH) ppm. $^{13}C\{^1H\}$ ([D_6]DMSO): δ = 26.66 (CH_3), 31.33 (CH_3), 115.00 (Ar–H), 122.05 (Ar–H), 123.45 (Ar–Cl), 131.00 (Ar–NH–N), 132.57 (C=N), 134.32 (Ar–SO_3 H), 141.24 (Ar–OH), 196.45 (C=O), 197.22 (C=O) ppm.

(H_2en)(HL) (2): Compound **1** (335 mg, 0.001 mol) was dissolved in ethanol (50 mL) and ethylenediamine (60 mg, 0.001 mol) was added. The mixture was stirred for 8 h at 70 °C giving a red precipitate of **2**, which was collected by filtration and recrystallized from ethanol to obtain crystals suitable for X-ray analysis. **2** is soluble in water, methanol, ethanol, and DMSO. $C_{13}H_{19}ClN_4O_6S$ (394.83): calcd. C 39.55, H 4.85, N 14.19; found C 39.24, H 4.53, N 14.11. IR (KBr): $\tilde{\nu}$ = 3926 [ν(NH)], 1652 [ν(C=O)], 1617 [ν(C=O···H)], 1560 [ν(C=N)], 739 [δ(CH, Ar)] cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 2.42 (s, 3 H, CH_3), 2.50 (s, 3 H, CH_3), 2.95 (s, 4 H, CH_2), 7.23–7.42 (2 H, Ar–H), 15.20 (s, 1 H, NH). $^{13}C\{^1H\}$ ([D_6]DMSO): δ = 28.61 (CH_3), 30.71 (CH_3), 48.39 (CH_2), 49.24 (CH_2), 114.54 (Ar–H), 116.42 (Ar–H), 123.64 (Ar–Cl), 132.18 (Ar–NH–N), 132.94 (C=N), 134.12 (Ar–SO_3^-), 151.10 (Ar-O-), 172.38 (C=O), 196.16 (C=O) ppm.

[Co(HL)(en)(H_2O)]·4H_2O (3). Method A: Compound **2** (790 mg, 0.002 mol) was dissolved in methanol (50 mL), $Co(NO_3)_2\cdot 6H_2O$ (582 mg, 0.002 mol) was added, and the mixture was stirred for 5 min and left to stand.

Method B: En (120 mg,0.002 mol) was added to a methanol solution (50 mL) of **1** (670 mg, 0.002 mol) and the mixture was heated to reflux for 10 min. $Co(NO_3)_2\cdot 6H_2O$ (582 mg) was added. In both cases, brown crystals of **3** separated from the reaction mixture after 4 d at room temperature, which were collected by filtration and dried in air; yield 41% (based on Co). $C_{13}H_{26}ClCoN_4O_{11}S$ (540.82): calcd. C 28.87, H 4.85, N 10.36; found C 28.75, H 4.94, N 10.45. IR (KBr): $\tilde{\nu}$ = 3508 [ν(OH)], 3437 [ν(NH)], 3211 [ν(NH)], 3102 [ν(NH)], 1652 [ν(C=O)], 1583 [ν(C=N)], 775 [δ(CH, Ar)] cm^{-1}.

[Cu(L)(Hen)(H_2O)] (4). Method A: Compound **2** (790 mg, 0.002 mol) was dissolved in methanol (50 mL), $Cu(NO_3)_2\cdot 2.5H_2O$ (466 mg, 0.002 mol) was added, and the mixture was stirred for 5 min and left to stand.

Method B: En (120 mg, 0.002 mol) was added to a solution of **1** (670 mg, 0.002 mol) in methanol (50 mL). The mixture was heated to reflux for 10 min before $Cu(NO_3)_2\cdot 2.5H_2O$ (466 mg, 0.002 mol) was added with stirring. The mixture was left to stand. In both cases the formation of a dark brown powder was observed after 4 d at room temperature. The powder was collected by filtration, dried in air, and recrystallized from an acetone/dimethylformamide (5:1, *v*/*v*) mixture; yield 47% (based on Cu). $C_{13}H_{19}ClCuN_4O_7S$ (474.4): calcd. C 32.98, H 3.83, N 11.84; found C 33.42, H 3.72, N 11.82. IR (KBr): $\tilde{\nu}$ = 3437 [ν(OH)], 3305 [ν(NH)], 3245 [ν(NH)], 3165 [ν(NH)], 3068 [ν(NH)], 1662 [ν(C=O)], 1638 [ν(C=O)], 750 [δ(CH, Ar)] cm^{-1}.

X-ray Structure Determination: Crystals of **2**–**4** were immersed in cryo-oil, mounted on a nylon loop, and measured at a temperature of 100 K. The X-ray diffraction data were collected with a Bruker AXS Smart ApexII Duo (for **2**, **3**) or a Nonius KappaCCD (for **4**) diffractometer using Mo-K_α radiation (λ = 0.710 73 Å). APEX2[18a] (for **2**, **3**) or Denzo–Scalepack[18b,18c] (for **4**) program packages were used for cell refinements and data reductions. The structures were solved by direct methods using the SHELXS-97[18d] program. A semiempirical (for **3**, **4**) or numerical (for **2**) absorption correction (SADABS)[18e] was applied to the data. The unit cell of **2** contained four water molecules of crystallization. Two of these molecules were disordered and partially lost. The final structure model was refined without the disordered water molecules. The contribution of these molecules to the calculated structure factors was taken into account using the SQUEEZE routine of PLATON.[18f] Because of the missing water molecules, the intermolecular H-bonding network in **2** is not realistic. The NH, NH_2, NH_3, and H_2O hydrogen atoms were located from the difference Fourier map but constrained to ride on their parent atom, with U_{iso} = 1.5 and U_{eq} (parent atom). Other hydrogen atoms were positioned geometrically and were also constrained to ride on their parent atoms, with C–H bond length in the range 0.95–0.99 Å, and U_{iso} = 1.2–1.5 U_{eq} (parent atom). Crystallographic data and selected geometric parameters are listed in Tables S1–S3 (see Supporting Information).

CCDC-809721 (for **2**), -809722 (for **3**), and 809723 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Potentiometric Measurements: The apparatus, general conditions, and methods of calculation are the same as those given in our previous work.[5c,8d] A mixture of **4** (23.7 mg,0.0500 mmol) and KCl (372.7 mg, 5.00 mmol) in water (50 mL) was titrated potentiometrically against standard water solutions of 0.01 M HCl or 0.01 M NaOH at 298 K.

Aerobic Oxidation of Alcohols in Aqueous Media: The reactions were carried out in 50 mL round-bottom flasks equipped with condensers under air at atmospheric pressure. Typically, to an aqueous solution of K_2CO_3 (5 mL, 0.1 M) were added alcohol (1.5 mmol), catalyst (0.015 mmol, 1 mol-% vs. substrate), and TEMPO (0.075 mmol, 5 mol-% vs. substrate). The reaction solutions were vigorously stirred using magnetic stirrers, and an oil bath was used to achieve the desired reaction temperature. After the oxidation reaction, reaction mixtures were neutralized by 1 M HCl, and then extracted into EtOAc (5 mL). The organic phase was used for chromatographic analyses using acetophenone as an internal standard.

Supporting Information (see footnote on the first page of this article): Synthesis and tautomeric equilibria, crystallographic data, atomic coordinates, bond lengths, bond angles, hydrogen bonds, the determination of the isoelectric point of **4**, and the quantitative determination of Cu^{II} with **1** and **2**. X-ray crystallographic data for **2**–**4** in CIF format.

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