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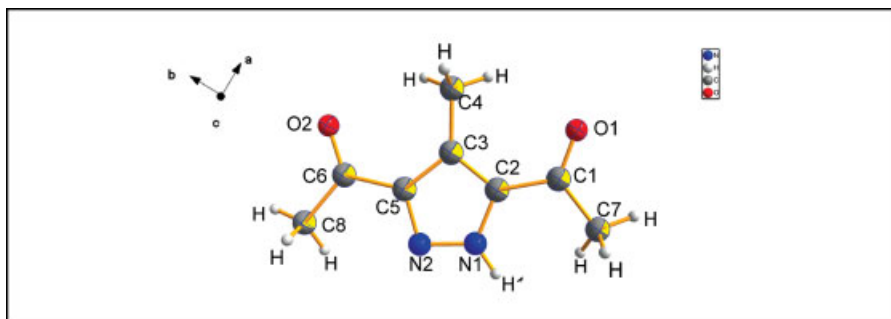
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The 3,5-diacetyl-4-methylpyrazole diketone has been synthesized and its crystal structure has been determined. This diketone reacts with hydroxylamine hydrochloride to give the dioxime derivative. This reaction, conducted in presence of copper II ions, leads to the formation of L_2M_2 copper II complexes.

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INTRODUCTION

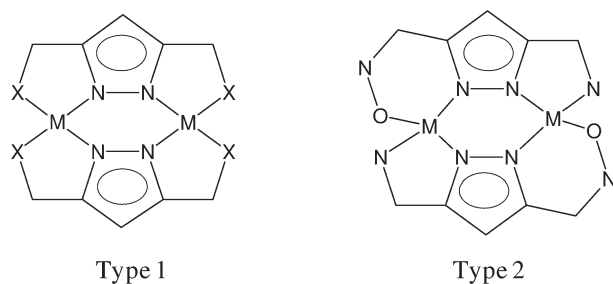
Research on transition metal complexes is a flourishing field with major interests focused on biological mimicry and cooperative phenomena in catalysis and magnetism. In this respect, pyrazole-based ligands have received a great deal of attention over the last decades due to their interesting coordination chemistry [1]. The pyrazole entity appears indeed particularly suited owing to its ability to bind simultaneously two metal centers in close proximity providing moreover an intramolecular pathway for spin-exchange interactions [2–9]. Further control of the metal–metal separation as well as the steric and electronic properties of the individual metal ions can be achieved by appropriate chelating side arms. Attached to the 3 and 5 positions of the heterocycle, these side arms are able to afford bis(μ -pyrazolato) bridged species L_2M_2 .

In most cases, e.g. in type 1 complexes, the chelated metal atoms form only five-membered rings involving the four nitrogen atoms of the two deprotonated pyrazole rings and the four chelating heteroatoms borne by the 3,5-substituted side arms as shown in Scheme 1 [4–9]. Interestingly, the use of functional groups such as oximes as chelating side arms has a singular attractiveness. Oximes are indeed not only generally easy to prepare but can also take advantage of two different bridg-

ing modes as shown in Scheme 1 (type 2). In type 2 complexes, the metal atom can bind either to the N atom, either to the deprotonated O-atom of the oxime moiety thus forming a six-membered ring. In this purpose, we have already employed pyridazine and pyrazolate units, such as 3,6-diformylpyridazines [10,11], 3,6-dibenzoylpyridazines [10], and 3,5-diacetyl-4-methylpyrazole [12] and related dioxime species. The synthesis, crystal structure, and magnetic properties of two binuclear copper (II) complexes of the 3,5-diacetyl-4-methylpyrazole dioxime ($dampdoH_3$), involving the two bridging modes of the oxime function has been also reported [13]. In the present study, we describe the synthesis and crystal structure of the 3,5-diacetyl-4-methylpyrazole ligand used in a new one-step preparation of L_2M_2 copper II complexes.

RESULTS AND DISCUSSION

The 3,5-diacetyl-4-methylpyrazole is prepared by the method of Wolff [12]. Reduced by Zn/H_2SO_4 , the isonitrosoacetylacetone (**2**) gives the aminoacetylacetone (**3**). This compound is then diazotized by sodium nitrite in acid medium (Scheme 2), affording the crude diazoacetylacetone (**4**) as an oily product which was in fact expected to be the 4-acetyl-5-methyl-oxadiazole (**4'**).

Scheme 1. L_2M_2 dinuclear complexes of pyrazolate anion.

To provide insight into the thermodynamics and kinetics of the possible internal cyclization of diazoacetylacetone (**4**) affording 4-acetyl-5-methyl-1,2,3-oxadiazole (**4'**), theoretical calculations were carried out at the B3LYP/6-31+g(d) DFT level. A thorough inspection of the frontier orbitals (HOMO and LUMO) of diazoacetyl-

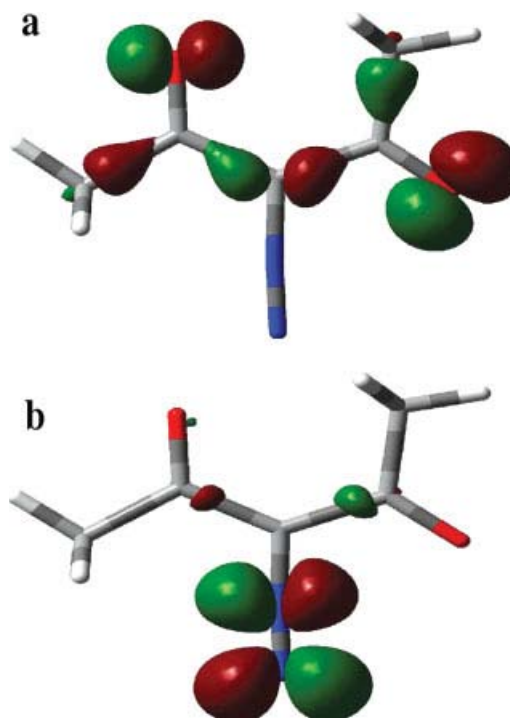
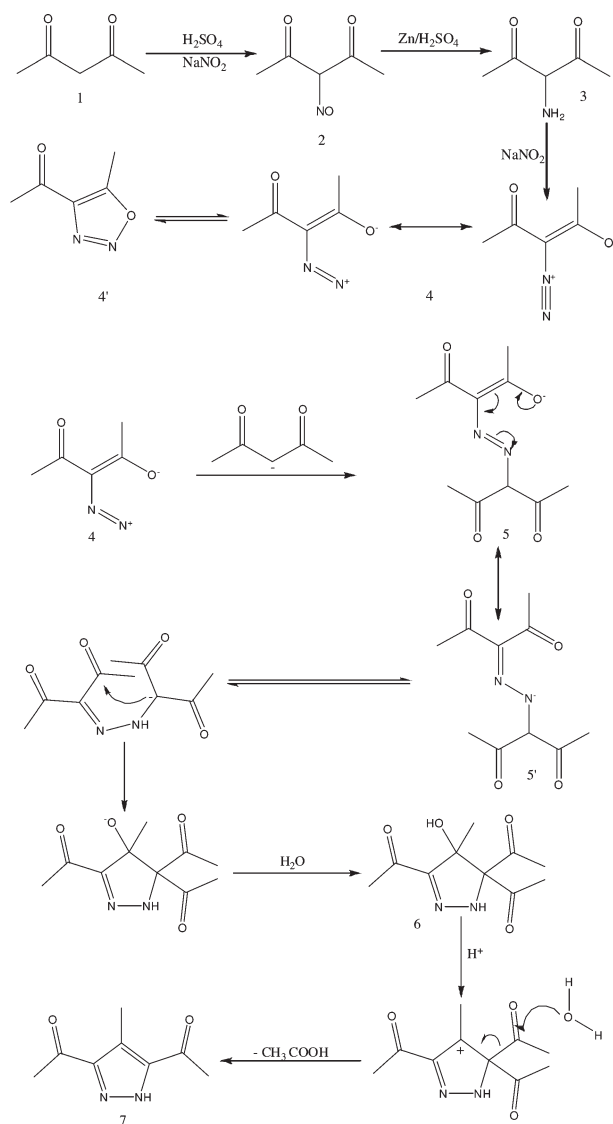
Scheme 2. Synthesis of 3,5-diacetyl-4-methylpyrazole.

Figure 1. Isodensity surface plots of the HOMO (a) and LUMO (b) for the lowest-energy gas-phase geometry of diazoacetylacetone (**4**). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

acetone (**4**) was first performed. The HOMO and LUMO for its most stable geometry in gas-phase show energy values of -7.5 and -2.7 eV, respectively. As depicted in Figure 1, the two frontier orbitals are distributed in the molecular plane. Although HOMO is mainly composed by lone pairs of the two carbonyl oxygen atoms, LUMO is an antibonding- π orbital located exclusively around the $N\equiv N$ triple bond. This orbital distribution suggests that the unique pathway for the internal cyclization of diazoacetylacetone (**4**) should reside in the attack of one of carbonyl oxygen atom lone pairs at the π -orbital located on the terminal nitrogen atom of the diazonium moiety.

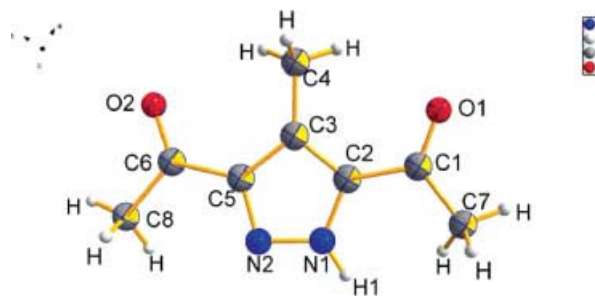


Figure 2. Perspective view of dampH structure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 3. Projection view of dampH structure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The optimized geometry for transition state joining compounds (**4**) and (**4'**) on the potential energy surface has a single imaginary frequency ($\nu_i = 163 \text{ cm}^{-1}$) corresponding to the stretching vibration of the forming N—O bond. The distance of the N—O forming bond in transition state geometry is 1.902 Å. The reaction from diazoacetylacetone (**4**) leading to the formation of oxadiazole (**4'**) is predicted slightly endothermic (+7.3 kcal/mol in gas-phase and 8.5 kcal/mol in water). Diazoacetylacetone (**4**) is then thermodynamically more stable than 4-acetyl-5-methyl-1,2,3-oxadiazole (**4'**).

Furthermore, the barrier height calculated from diazoacetylacetone (**4**) is 8.0 kcal/mol (9.3 kcal/mol in water) indicating that formation of 4-acetyl-5-methyl-1,2,3-oxadiazole (**4'**) is not kinetically favored, at least at ambient temperature. This product is thus very unstable and must react immediately with carbanion of the 2,4-pentanedione as previously described [14]. This condensation and the subsequent heterocyclization give a pyrazoline (**6**), which was not isolated. In aqueous acidic medium, this compound gives the pyrazole (**7**) after elimination of acetic acid as described in Scheme 2. Slow evaporation of an ethanolic solution of **7** gives finally single crystals suitable for X-ray diffraction.

The main features of the crystal structure of compound dampH (**7**) result from the planarity of the whole entity (Figs. 2 and 3).

The crystal structure is formed by layers of planar dampH molecules stacked along the axis *c* direction.

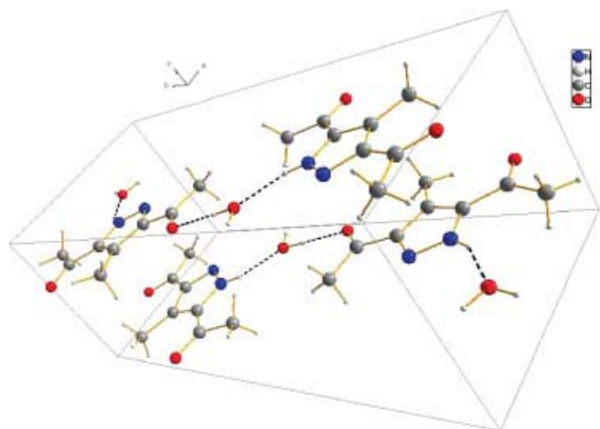
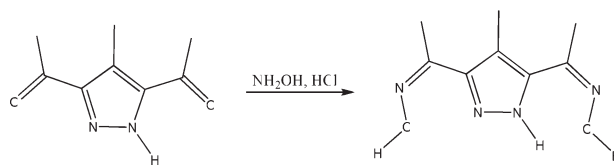


Figure 4. View of dampH crystal structure with its stabilizing hydrogen bond network (dashed lines). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Scheme 3. Synthesis of dampdoH₃.



The layered crystal structure is also stabilized by an intermolecular hydrogen bond network forming dimeric ligand associations. The hydrogen bond interactions between two coplanar and adjacent 3,5-diacetyl-4-methylpyrazole ligands are mediated by a water molecule. The oxygen atom O3 of this water molecule gives an hydrogen bond with the hydrogen atom H1 bound to the nitrogen atom of pyrazole ring in the first ligand (O3—H1 = 1.9571 Å). Furthermore, one of the two hydrogen atoms H1w of the water molecule is also involved in a second hydrogen bond interaction with the oxygen atom O2 of the ketonic function of the second ligand molecule (H1w—O1 = 1.9207 Å) (Fig. 4).

This diketone (**7**) reacts with hydroxylamine hydrochloride to give the diacetyl dioxime derivative (dampdoH₃) as described in Scheme 3. On reaction with copper II cations dampdoH₃ leads to the bis(μ -pyrazolato) bridged L₂M₂ species [13] as described in Scheme 4, with L = dampdoH.

From dampdoH₃ (H₂L) and CuCl₂·6H₂O, two structurally isomeric complexes [Cu₂(HL)₂Cl₂]·6H₂O, which differ only from the hydrogen bonding, were previously obtained [10]. One of these complexes can be obtained directly from **7** by a one-step reaction with copper II ions in the presence of hydroxylamine hydrochloride. This reaction using CuCl₂, CuClO₄, Cu(NO₃)₂, or CuSO₄, leads, after several days, to the formation of dark green crystals of the copper II complexes previously described [13]. In this complex, the axial ligand is a chloride ion even in presence of perchlorate, nitrate, or sulphate ions, indicating that chloride ions are better complexing species.

Scheme 4. Dinuclear complex of Cu₂(HL)₂²⁺.

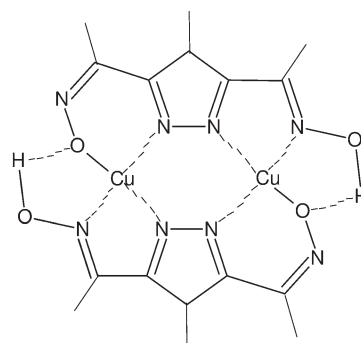


Table 1

Summary of the crystal data and structure refinement for dampH.

Formula	C ₈ H ₁₂ N ₂ O ₃
Formula weight (g/mol)	184.2
Crystal system	Orthorhombic
Space group	Pbcm
<i>a</i> (Å)	<i>a</i> = 7.7798 (10)
<i>b</i> (Å)	<i>b</i> = 18.337 (3)
<i>c</i> (Å)	<i>c</i> = 6.7735 (11)
$\alpha = \beta = \gamma$ (°)	90
<i>V</i> (Å ³)	966.3 (2)
<i>Z</i>	4
<i>D</i> _{cal} (mg m ⁻³)	1.266
<i>T</i> (K)	296
<i>F</i> (000)	392
Crystal size (mm)	0.180 × 0.254 × 0.628
μ (mm ⁻¹)	0.098
Range of indices	<i>h</i> , -11 to 11; <i>k</i> , -26 to 23; <i>l</i> , -9 to 9
Reflections measured	13460
<i>R</i> _{int}	2.64
(<i>R</i> _{all} ; <i>R</i> _{2σ})	7.43; 4.89
(<i>wR</i> _{all} ; <i>wR</i> _{2σ})	15.96; 14.08
Number of parameters	88
Maximum peak in final ΔF map (e ^Å ⁻³)	0.28
Minimum peak in final ΔF map (e ^Å ⁻³)	-0.15

EXPERIMENTAL

Melting points were determined on an IA 9000 series Electrothermal apparatus and are uncorrected. Elemental analyses of C, H, N, and S were performed at the Elemental Analysis service of CNRS, Vernaison, France. ¹H and ¹³C NMR spectra were recorded on a Bruker F.T. AC 300 spectrometer (300 MHz for ¹H NMR and 75 MHz for ¹³C NMR) using chloroform (CDCl₃) as solvent. Matrix-assisted laser desorption ionization (MALDI) and time-of-flight mass spectrometry (TOF-MS) are used to record the mass spectra of the correspondent compounds. All starting materials were of reagent grade and were used as purchased.

All theoretical calculations were performed using the Gaussian 03 suite of programs [15]. The gas-phase geometries of diazoacetylacetone (**4**), 4-acetyl-5-methyl-1,2,3-oxadiazole (**4'**), and related transition state were optimized using hybrid density functional theory (B3LYP) [16] and the 6-31+g(d) basis set. Frequency calculations were used to verify the nature of the computed stationary points. Geometries obtained for **4** and **4'** were real minima with all real vibrational frequencies while that of transition state was indeed a first-order saddle point with a single imaginary frequency. To ensure that the transition state joins the two compounds (**4**) and (**4'**) on the potential energy surface, an intrinsic reaction coordinate (IRC) [17] analysis was performed. Frequency calculations also allowed us to calculate the zero-point energy (ZPE) corrections, which were finally added to electronic energies. The energies computed in water include the ZPE-corrected electronic energy plus the solvation energy as obtained from the polarizable continuum model (PCM) [18].

Single crystals of 3,5-diacetyl-4-methylpyrazole hydrated (dampH) were obtained in the form of brown needles, by slow evaporation at room temperature in aqueous solution of

Table 2

Bond distances (Å) and angles (°) for dampH.

Bond distances			
N1—N2	1.327(2)	C3—C4	1.492(2)
N2—C5	1.351(2)	C5—C3	1.407(2)
N1—C2	1.363(2)	C5—C6	1.476(2)
C1—C7	1.498(3)	C6—O2	1.225(2)
C1—C2	1.468(2)	C6—C8	1.490(3)
C2—C3	1.395(2)	O1—C1	1.209(2)
Angles			
N2—N1—C2	113.0(1)	C2—C3—C4	128.0(1)
N1—N2—C5	104.6(1)	C5—C3—C4	128.5(1)
O1—C1—C2	120.1(1)	N2—C5—C3	112.1(1)
O1—C1—C7	121.8(2)	N2—C5—C6	118.4(1)
C2—C1—C7	118.1(2)	C3—C5—C6	129.5(1)
N1—C—C1	122.1(1)	O2—C6—C5	120.4(2)
C3—C2—C1	131.1(1)	C5—C6—C8	117.8(1)
N1—C2—C3	106.8(1)	O2—C6—C8	121.8(2)
C2—C3—C5	103.5(1)		

dampH. A single crystal of compound **7** was mounted on a Bruker AXS SMART three-circle diffractometer using graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å), equipped with a CCD 4K two-dimensional detector [19]. A total of 1653 independent reflections were collected in the range of $2.22 < \theta < 31.03$ with *R*_{int} = 2.64. Data were corrected for Lorentz and polarization using program SaintPlus (Table 1). Atomic positions were determined using SHELXS [20] and refined using full matrix least squares [21]. Hydrogen positions were calculated and included in the final cycles of refinement in constrained positions and with fixed isotropic

Table 3

Atomic coordinates and equivalent displacement for dampH.

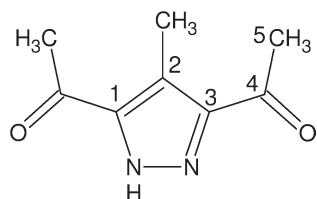
Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (Å ²)
N1	0.6307(2)	0.15617(7)	1/4	0.0547(4)
N2	0.5408(2)	0.21765(7)	1/4	0.0557(4)
C1	0.9273(2)	0.10700(9)	1/4	0.0610(5)
C2	0.8038(2)	0.16751(8)	1/4	0.0521(4)
C3	0.8288(2)	0.24286(9)	1/4	0.0501(4)
C4	0.9949(2)	0.28354(9)	1/4	0.0599(5)
C5	0.6606(2)	0.27101(8)	1/4	0.0507(4)
C6	0.6021(2)	0.34760(9)	1/4	0.0570(5)
C7	0.8583(3)	0.03073(9)	1/4	0.0774(7)
C8	0.4134(3)	0.36152(9)	1/4	0.0828(7)
O1	0.0799(2)	0.11936(9)	1/4	0.1014(7)
O2	0.07067(2)	0.39751(6)	1/4	0.0772(5)
O3	0.3918(2)	0.04499(7)	1/4	0.0941(7)
H _{N1}	0.5845	0.1136	1/4	0.0660
H _{C4}	0.9853	0.3255	0.1660	0.0900
H _{C4}	0.0848	0.2524	0.2020	0.0900
H _{C4}	0.0215	0.2989	0.3820	0.0900
H _{C1}	0.3566	0.3249	0.1725	0.1240
H _{C1}	0.3910	0.4087	0.1945	0.1240
H _{C1}	0.3710	0.3599	0.3830	0.1240
H _{C6}	0.8124	0.0195	0.3780	0.1160
H _{C6}	0.9492	-0.0028	0.2191	0.1160
H _{C6}	0.7689	0.0266	0.1528	0.1160
H _{w1}	0.363(3)	-0.002(2)	1/4	0.089(8)
H _{w2}	0.294(4)	0.067(2)	1/4	0.101(9)

Table 4
Anisotropic displacement parameters for dampH.

	U11	U22	U33	U12	U13	U23
N1	0.0412(7)	0.0322(6)	0.0907(11)	0.0037(5)	0	0
N2	0.0408(6)	0.0358(6)	0.0905(11)	0.0018(5)	0	0
C1	0.0485(9)	0.0408(8)	0.0935(14)	0.0056(7)	0	0
C2	0.0418(8)	0.0353(7)	0.0794(12)	0.0010(6)	0	0
C3	0.0388(7)	0.0364(7)	0.0752(11)	0.0033(6)	0	0
C4	0.0405(8)	0.0453(9)	0.0939(13)	0.0089(6)	0	0
C5	0.0407(7)	0.0330(7)	0.0786(11)	0.0024(5)	0	0
C6	0.0481(8)	0.0353(8)	0.0876(13)	0.0012(6)	0	0
C7	0.0737(13)	0.0366(9)	0.1218(19)	0.0058(8)	0	0
C8	0.0491(10)	0.0503(10)	0.0149(2)	0.0116(8)	0	0
O1	0.0444(7)	0.0057(8)	0.0204(2)	0.0107(6)	0	0
O2	0.0588(8)	0.0342(6)	0.1385(14)	0.0035(5)	0	0
O3	0.0448(7)	0.0333(7)	0.0204(2)	0.0008(5)	0	0

thermal parameters. Absorption corrections were not made due to the small value of the absorption coefficients (Table 1). Extinction was refined for all the three structures but was minimal. Figure 2 shows a perspective view of this compound with the numbering scheme, while in Table 2 bond distances and angles in the molecule (dampH) are reported. Atomic coordinates and equivalent displacement for dampH are reported in Table 3; anisotropic displacement parameters for dampH are reported in Table 4.

General procedure for the synthesis of compounds 1, 4, and 7. Starting material acetylacetone (**1**) was commercialized. The formula of the parent compounds with corresponding numbers to carbons scheme is given below.



Synthesis of isonitroacetylacetone (2). A suspension of acetylacetone (**1**) (50 g, 0.5 mol) in 7% sulphuric acid (500 mL) was stirred until it was completely dissolved. Sodium nitrite (35 g, 0.5 mol) in water (150 mL) was added, and the stirring was continued for 90 min. The reaction mixture was extracted with ether, dried (magnesium sulfate), filtered, and evaporated. The solid was recrystallized from ethanol: mp 75°C, yield 50 g, 77.5%.

Synthesis of the acetylacetonate diazonium (4). Isonitroacetylacetone **2** (10 g, 0.07 mol) dissolved in 30% sulphuric acid (100 mL) was cooled under 0°C. Zinc powder (15 g, 0.23 mol) was added, and the reaction mixture was allowed for 15 min. The limpid solution was filtered and diluted with water. A solution of sodium nitrite (6 g, 0.085 mol) in water (30 mL) was added and cooled. The reaction mixture was extracted with ether, and treated with 5% sodium carbonate. The residue was dried (magnesium sulfate), filtered, and evaporated to give an oil product: yield 4 g, 45%. The

crude powder was used for the next step for the synthesis without further purification.

Synthesis of 3,5-diacetyl-4-methylpyrazole (7). A mixture of the acetylacetonate diazonium (**4**) (2 g, 0.016 mol), acetylacetone (**1**) (1.6 g, 0.015 mol), and sodium hydroxide (0.6 g, 0.015 mol) in water (30 mL) was heated at 50°C for 90 min. The resulting solution was concentrated under vacuum using a rotatory evaporator. After cooling, the obtained solution was neutralized by slow addition of aqueous sulfuric acid solution (0.5M). The obtained solid was filtered and recrystallized from ethanol: mp 112°C; yield 2 g, 75 %; ¹H NMR (CDCl₃) δ (ppm) 10.78 (s, 1H); 2.51 (s, 6H); 2.46 (s, 3H); ¹³C NMR (CDCl₃) δ (ppm) 192.96; 144.94; 121.58; 28.57; 10.21. MALDI-TOFMS: *m/z* 167 (M + 1). Anal. Calcd for C₈H₁₀N₂O₂: C, 57.82; H, 6.08; N, 16.86. Found: C, 58.02; H, 5.98; N, 16.75.

Synthesis of 3,5-diacetyl-4-methylpyrazole dioxime. A solution of hydroxylamine hydrochloride (1.4 g, 20 mmol) and NaOH (0.8 g, 20 mmol) in methanol/water solution (in ratio 50:50) was added to a solution of 3,5-diacetyl-4-methylpyrazole (1.5 g, 9 mmol) in water (20 mL) and heated under reflux for 2 h. After cooling, the solid product was filtered and recrystallized from ethanol: mp 218°C; yield 81%; ¹H NMR (DMSO-d₆) δ (ppm) 12.96 (s, H, NH); 11.33 (s, 1H, OH); 10.97 (s, 1H, OH); 2.27 (s, 3H); 2.14 (s, 6H); ¹³C NMR (DMSO-d₆) δ (ppm) 150.39; 141.51; 134.62; 111.88; 11.70. MALDI-TOFMS: *m/z* 197 (M + 1). Anal. Calcd for C₈H₁₂N₄O₂: C, 48.97; H, 6.16; N, 28.56. Found: C, 49.02; H, 5.98; N, 28.78.

Preparation of complexes. A solution of copper II chloride dehydrate (85 mg, 0.5 mmol) and hydroxylamine hydrochloride (69,5 mg, 1 mmol) in water (20 mL) was added to a solution of dampH (92 mg, 0.5 mmol) in ethanol (10 mL) and heated under reflux a few minutes. The mixture was filtered to remove any precipitated material. Slow evaporation at room temperature during 3 days affords dark green crystals which were filtered, washed with water and dried in vacuo. The crystals were found to have the formula [Cu₂(dampdoH)₂Cl₂·H₂O] yield 110 mg; 70%. Anal. Calcd: C, 30.75; H, 4.20; Cl, 11.35; Cu, 20.35; N, 17.95; O, 15.40 Found: C, 30.69; H, 4.21; Cl, 11.37; Cu, 20.29; N, 18.00; O, 15.44.

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