

N-tripodal ligands to generate copper catalysts for the syndiotactic polymerization of methyl-methacrylate: Crystal structures of copper complexes

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Abstract

A library of *N*-tripodal ligands, based on a central nitrogen atom connected to three different functionalized arms, was investigated via a parallel approach for the polymerization of methyl-methacrylate (MMA) in presence of late transition metal salts. Copper salts CuCl_2 and $\text{Cu}(\text{OAc})_2$ in combination with *N*-(2-furanylmethyl)-*N*-(1-3,5-dimethyl-1H-pyrazolylmethyl)-*N*-(phenylmethyl)amine were detected as efficient catalysts for the syndiotactic polymerization of MMA ($[\text{rr}]$ up to 78%). Kinetic studies and X-ray structures of the best catalysts were reported.

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1. Introduction

Polymethyl-methacrylate (PMMA) is almost exclusively produced in industry via radical polymerization with an annual world production greater than two million tons. This PMMA is generally atactic. The glass transition temperature (T_g) and others properties are very dependent on tacticity. T_g of isotactic PMMA is about 65 °C, whereas syndiotactic PMMA exhibits a higher T_g , about 140 °C. The advantage of the high optical quality of PMMA is far improved when the T_g is raised. That is why many attempts aiming to increase the syndiotacticity of PMMA were planned [1,2]. Non radical metal-mediated polymerization of methyl-methacrylate (MMA) was first described at the beginning of the 1990s when two groups independently reported the living syndiospecific polymerization of MMA with d^0/f^n metallocene catalysts: Yasuda et al. used a neutral single-component lanthanide-based catalyst

($[\text{Cp}_2^*\text{SmH}]_2$) to produce highly syndiotactic PMMA ($[\text{rr}] = 95\%$) with high yield [3]. Collins et al. achieved the controlled polymerization of MMA with a two-component system consisting of a cationic zirconocenium complex $\text{Cp}_2\text{ZrMe}(\text{THF})^+\text{BPh}_4^-$ and a neutral zirconocene Cp_2ZrMe_2 with a lower amount of syndiotactic dyads ($[\text{rr}] = 80\%$) [4]. Since then, important research has been conducted with late transition metal-mediated polymerization, especially nickel-based catalysts: $\text{Ni}(\text{acac})_2$ -MAO was first found to be an effective catalyst for the atactic polymerization of MMA [5,6]. Syndiotactic PMMA ($[\text{rr}] = 72\%$) produced via late transition metal catalysts was first described with Cp_2Ni -MAO [7]. Late transition metal complexes such as (α -diimine)nickel(II), (pyridyl bis-imine)iron(II) and (pyridyl bis-imine)cobalt(II), which are widely used for the polymerization of olefins, were also reported to polymerize MMA in combination with MAO to give slightly syndiotactic PMMA ($[\text{rr}] = 62$ – 71%) [8]. Recently, Carlini et al. reported that salicylaldiminatenickel(II) complexes could polymerize MMA to give syndiotactic rich PMMA ($[\text{rr}] = 77\%$) with a relatively wide molecular weight distributions after activation with MAO

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[9–11]. Nickel(II) bearing β -ketimino ligands [*N, O*] were recently reported to polymerize MMA to give syndiotactic rich PMMA ($[\text{rr}] = 82\%$) with a relatively broad molecular weight distribution after activation with MAO [12,13]. However, very few examples of copper-based catalysts activated by MAO are reported in the literature. The Cu(D-MOX)Cl₂/MAO [14] and Cu-bis(benzimidazole) [15,16] systems were described as efficient catalysts for the polymerization of methacrylates but the resulting polymers were atactic. Here, we report new and highly active copper-based catalysts based on *N*-tripodal ligands for the syndiospecific polymerization of MMA. Precatalysts were isolated and described by X-ray diffractometry.

2. Results and discussions

The design of new ligands able to give selective mono, bi or tridentate coordination with transition metals is a current challenge in the field of controlled polymerization. In previous papers, we have reported new heterocyclic multidentate molecules as promising ligands in coordination chemistry and organometallic catalysis [17]. These *N*-tripodal molecules are easily accessible and are based on a central nitrogen connected with three different functionalized arms. Tripodal ligands can be obtained via the condensation of 1-hydroxymethyl pyrazoles or 1-hydroxymethyl triazoles with heterocyclic secondary amines using microwaves [18]. All derivatives **1a–g** (Fig. 1) were obtained with very high yield and purity without any purification process. It was considered that, due to the diversity of the arms, this class of molecules would present a high potential for polymerization as they can potentially coordinate transition metals in different ways, i.e. mono, bi or tridentate fashion. In addition, they have never been used in conjunction with late transition metals to polymerize methacrylates. The number of possible coordination between

ligands **1a–g** and different metal salts is very high depending on the metal centers, the counteranion and the nature and position of heteroatoms within these molecules. Thus, we have used a parallel approach to test catalytic systems for the polymerization of MMA. The synthesis of the library of potential catalysts with a combination of different metal salts (**M**) and tripodal ligands **1a–g** (**L**) using a 96 well-plate format was then achieved. The complexation reactions were performed in tetrahydrofuran (THF) at room temperature for 2 h with usual and unusual metallic precursors having a potential in catalysis (CrCl₃, CoCl₂, FeCl₂, FeCl₃, (COD)PdCl₂, Cu(OAc)₂, CuCl₂, (DME)-NiBr₂, [Ni(π -allyl)Cl]₂, [(*p*-cym)RuCl₂]₂, [(nbd)RhCl]₂). After drying the solutions, polymerizations of MMA in toluene were carried out at room temperature for 4 h under argon atmosphere. No activity was observed without activation with MAO. When they were activated with MAO, ligands **1a**, **1b**, **1f** and **1g** in conjunction with copper dichloride or copper acetate gave a gel, whereas cobalt, iron, palladium, nickel, ruthenium and rhodium catalysts gave little or no activity. Since copper precursors CuCl₂ and Cu(OAc)₂ alone do not provide any polymer after activation with MAO, the three component mixture [copper(II)/ligands/MAO] is thus essential to obtain PMMA. These systems were then evaluated in a SCHLENK scale (Table 1). With the experimental conditions used, Cu(OAc)₂-based catalysts give yields from 23% to 40% and produce a PMMA with a high degree of syndiotacticity ($[\text{rr}] = 73\text{--}78\%$). CuCl₂ associated with ligands **1b** and **1g** gives higher yields up to 60% and produces a polymer with a high degree of syndiotacticity ($[\text{rr}] = 72\text{--}75\%$). The ligands **1b** and **1g** are very similar with the same dimethyl-pyrazole group, and with a furan or thiophen group. Nevertheless, CuCl₂/**1b** with furan moiety produces a PMMA with number average molecular weight (M_n) measured at 73400 g/mol whereas CuCl₂/**1g** with thiophen moiety produces a

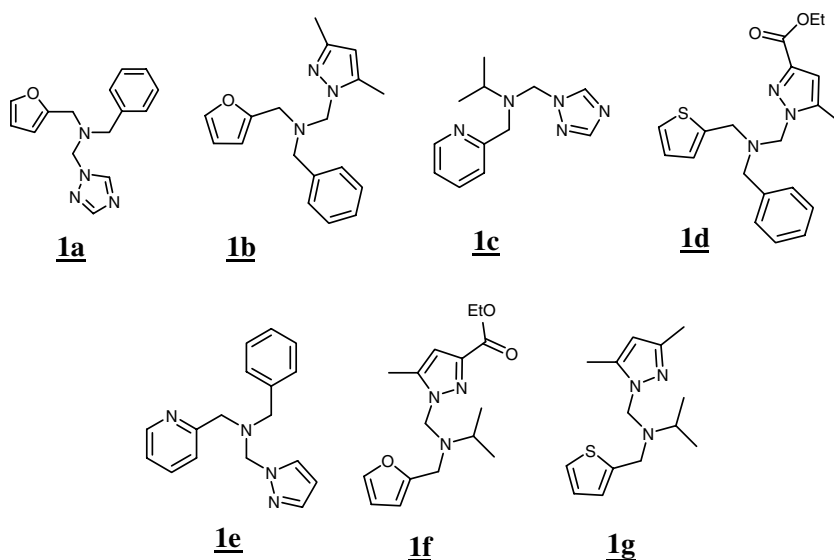


Fig. 1. Library of *N*-tripodal ligands.

Table 1
Polymerization of MMA with active M/L catalysts

Catalysts M/L ^a	Temp. (°C)	Cu/MAO (mol/mol)	Yield (%) ^b	M_n^c	I_p^c	Tacticity (%) ^d			T_g (°C) ^e
						rr	mr	mm	
CuCl ₂ /1b	30	1/20	64	73 400	1.85	72	20	8	128
CuCl ₂ /1g	30	1/20	57	149 300	1.95	75	18	7	126
Cu(OAc) ₂ /1b	30	1/20	31	339 200	3.16	78	15	7	124
Cu(OAc) ₂ /1d	30	1/20	23	725 650	1.84	77	16	7	125
Cu(OAc) ₂ /1f	30	1/20	27	53 120	1.95	75	16	9	123
Cu(OAc) ₂ /1g	30	1/20	40	47 820	4.86	73	17	10	122
CuCl ₂ /1b	0	1/20	12	58 300	2.07	62	23	15	119
	30	1/20	64	73 400	1.85	72	20	8	128
	50	1/20	74	114 602	2.13	72	21	7	127
	30	1/100	34		^f	^f	55	29	16

^a Complexation M/L = 1/2, RT, 2 h, THF, [M] = 0.1 M.

^b Polymerization condition: M/MAO/MMA = 1/20/1000, 30 °C, 4 h, MMA:toluene = 1:2 in vol., yield defined as mass of dry polymer recovered/mass of monomer used.

^c Determined by means of GPC.

^d Determined by ¹H NMR analysis.

^e Determined by means of DSC.

^f Trimodal distribution of molecular weights M_p = 86 600, 7130 and 540.

PMMA with a M_n two times higher, 149 300 g/mol. In both cases broad molecular weight distribution were observed (I_p = 1.85–1.95). Table 1 gives lots of information. However, it is not easy to explain the difference of activity and selectivity induced by ligands 1a–g as they are differentiated by at least two different arms. In addition, the counteranion (OAc⁻/Cl⁻) seems to have the largest effect.

Catalyst CuCl₂/1b was evaluated more in detail for the polymerization of MMA by changing the temperature of polymerization and the amount of MAO. No significant improvement in syndiotacticity could be achieved: The same degree of syndiotacticity is obtained at 50 °C, whereas a decrease in the temperature to 0 °C leads to a decrease in syndiotacticity ([rr] = 62%). A kinetic study was also carried out with these catalytic systems based on CuCl₂. For such systems the rate of polymerization could be expressed as $R_p = -d[MMA]/dt = k_p[MMA]^a \cdot [\text{active center}]^b$, where k_p is the propagation rate constant, and a

and b are the kinetic orders of the monomer and the active centers, respectively [6]. Fig. 2 (left) shows the semi-logarithmic plot of the conversion of MMA as a function of time at 0 and 20 °C. As expected, the rate of consumption of MMA increases at higher temperature. Interestingly, a linear regime is observed for both traces which indicates (a) a first-order MMA conversion and (b) the concentration of the active centers was constant during the first 30–40% of the conversion, which is in good agreement with the quasi steady-state approximation. One can see at 20 °C a deviation from linearity of the semi-logarithmic trace after 30% of conversion. Changes in M_n and the polydispersity index (I_p) in function of MMA conversion are also plotted in Fig. 2 (right). With the same M/MAO/MMA ratios, M_n remains the same about 60 000–70 000 g/mol while the I_p remains quite high in both cases (>2). Repo et al. also observed no evolution of M_n during the polymerization of *tert*-butyl acrylate with iron(II) bearing

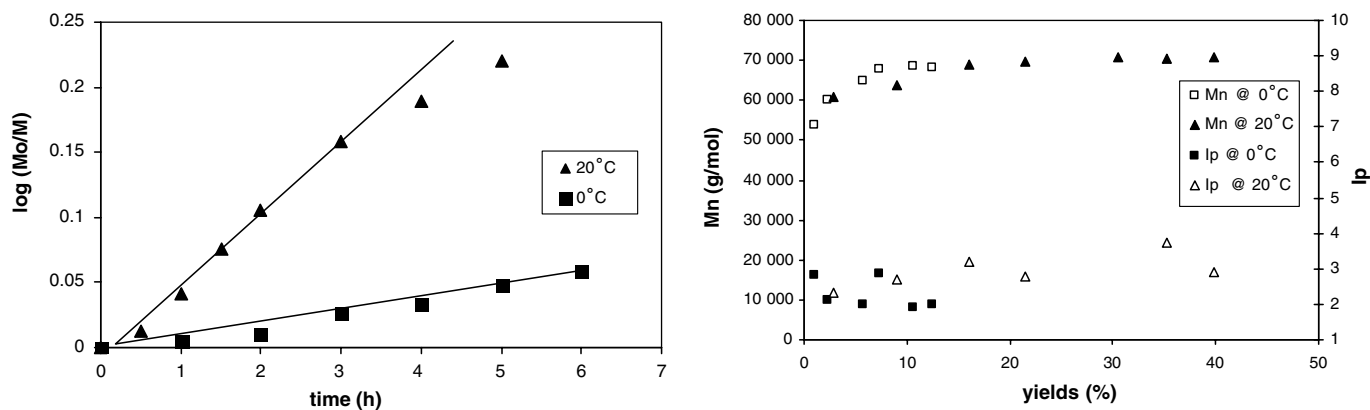


Fig. 2. Semi-logarithmic plots as a function of time at 0 °C and 20 °C (left), molecular weight and polydispersity index obtained by GPC from aliquots withdrawn during the polymerization as a function of MMA conversion (right). Conditions [CuCl₂/1b]/MAO/MMA = 1/20/1000, MMA:toluene = 1:2 in vol.

bis(imido)pyridyl or phosphine ligands activated with MAO [19]. Such characteristics indicate there is no control of molecular weight. From these initial rates of polymerization, one can plot the Arrhenius trace and calculate the overall activation energy, about 50 kJ/mol. This value could not be directly compared with another one from a copper-based catalyst, but it is much higher than the one published by Endo et al. (15.0 kJ/mol with Ni(acac)₂-MAO catalyst for the polymerization of MMA) [6].

Interestingly, CuCl₂ and Cu(OAc)₂ in conjunction with ligand **1b** give different results from the point of view of M_n and I_p . Cu(OAc)₂/**1b** give higher M_n than CuCl₂/**1b** (339200 and 73400 respectively), but higher I_p ($I_p = 3.16$ and 1.85, respectively). Moreover, syndiotacticity observed with Cu(OAc)₂/**1b** is the highest ($[rr] = 78\%$). Single crystals suitable for X-ray structure determination of copper complexes CuCl₂/**1b** and Cu(OAc)₂/**1b**, were obtained from recrystallisation in THF/heptane (1/2 in vol.). As depicted in Fig. 3, the air-stable compound CuCl₂/**1b** is a distorted tetrahedral complex, where ligand **1b** is bidentate. Coordination of copper occurred via the sp² nitrogen of the pyrazole and the central sp³ nitrogen, and two chlorine atoms acting as monodentate ligands. The furan unit does not participate to the coordination. Distance between central nitrogen and the copper center is 2.089 Å which is common for copper dichloride complexes with *N,N*-bichelating ligands for instance Cu(DMOx)Cl₂ ($d(\text{Cu}-\text{N}) = 1.994$ Å) [14]. Distance between the pyrazole unit and copper center is 1.959 Å for complex CuCl₂/**1b**. This is a little shorter than other complexes with tripodal ligand containing pyrazol unit [20–22]. However, tri or tridentate coordination mode were observed for these latter complexes, which is different from the bidentate fashion observed for complex CuCl₂/**1b**. When associated with Cu(OAc)₂, ligand **1b** leads

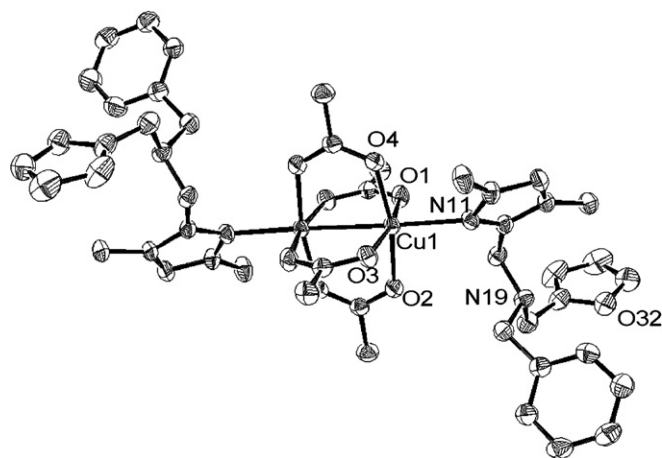


Fig. 4. Molecular structure of pre-catalyst Cu(OAc)₂/**1b**; Selected bond lengths (Å) and angles (°): Cu₁-N₁₁ 2.234, Cu₁-Cu₁^{*} 2.679, Cu₁-O₁ 1.980, Cu₁-O₂ 1.973, Cu₁-O₃ 1.984, Cu₁-O₄ 1.976, N₁₁-Cu₁-Cu₁^{*} 176.64, N₁₁-Cu₁-O₁ 92.66, N₁₁-Cu₁-O₂ 97.09, N₁₁-Cu₁-O₃ 99.64, and N₁₁-Cu₁-O₄ 95.48.

to the formation of a completely different coordination mode. As depicted in Fig. 3, X-ray analysis revealed that four acetate ligands bridge copper centers in a μ -mode leading to a paddle wheel type copper acetate. Two tripodal ligands acting as monodentate ligands bind the axial sites of the copper centre through the sp² nitrogen atom of the pyrazole unit with a Cu₁N₁₁ distance of 2.234 Å. An inversion centre lies on the midpoint of the copper centre then the complex Cu(OAc)₂/**1b** is centrosymmetric. The distance of Cu₁-Cu₁^{*} is 2.679 Å and the angle N₁₁-Cu₁-Cu₁^{*} is 176.64° and is nearly linear. This copper dimer conformation was already obtained from Cu(OAc)₂ salt and N containing ligands such as pyrazine [23] or triazol based ligand ($d(\text{Cu}-\text{N}) = 2.167$ Å) [24]. It is interesting to note that acetate (OAc) are able to induce an anion-templating effect (paddle wheel μ mode) in the solid state (see Fig. 4). This effect should be destroyed in solution in the presence of MAO to induce a different coordination mode (di- or tridentate) than the monodentate fashion to explain the syndiospecific polymerization observed.

In conclusion, we have reported a new class of ligands for the syndiotactic polymerization of MMA in presence of copper salts. Further research is currently being conducted in order to determine the polymerization mechanism and correlate the structure of active catalysts and high syndiotacticity.

3. Experimental

All experiments were carried out under controlled atmosphere using standard SCHLENK techniques or glove box. Solvents were distilled over standard drying agents under nitrogen and degassed directly before used. MMA from Aldrich (99%) was distilled over CaH₂ under reduced pressure. Compounds **1a-g** were prepared with high purity according to published methods [16]. Crystallographic data

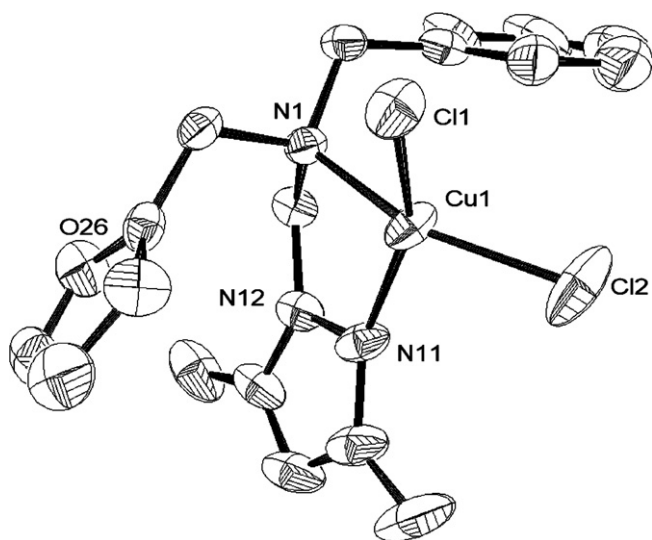


Fig. 3. Molecular structure of pre-catalyst CuCl₂/**1b**; Selected bond lengths (Å) and angles (°): Cu₁-N₁ 1.962, Cu₁-N₁₁ 2.084, Cu₁-Cl₂ 2.227, Cu-Cl₁ 2.219, N₁-Cu₁-N₁₁ 82.43, N₁-Cu₁-Cl₁ 94.55, N₁₁-Cu₁-Cl₂ 99.17, and Cl₁-Cu₁-Cl₂ 96.16.

collection, unit cell constant and space group determination were carried out on an automatic 'Enraf Nonius FR590' NONIUS Kappa CCD diffractometer with graphite monochromatized Mo K α radiation at 120 K. The cell parameters are obtained with Denzo and Scalepack with 10 frames (psi rotation: 1° per frame). The structure is solved with SIR-97. The whole structure is refined with SHELXL97 by the full-matrix least-square techniques.

3.1. Screening test

10 μ moles of each metal salt were added in 2.5 ml of THF and stirred until complete dissolution, then 24 μ moles of each ligand were added in 3 mL of THF. 1 mL-tubes were disposed in a 96 well-plate. The metal salts were disposed in columns 1–11 and the ligands in rows B–H. Each tube (from column 1 to 11) was charged first with 100 μ L of the appropriate metal salt solution (0.4 μ mol). Then, each tube (from rows A to G) was charged with 100 μ L of a solution of the corresponding ligand (0.8 μ mol). The cell in A-12 was kept empty. The mixtures were let to react during 2 h at room temperature. Then, the solvent was evaporated under reduced pressure and the catalysts were used without further purification for the polymerization. 1.8 μ L of MAO (30% wt in toluene) were added in all tubes, and after 25 min at room temperature, 100 μ L of toluene and 43 μ L of MMA were added in each tubes. Then, the tubes were sealed and carefully stirred by hand. After 4 h at 30 °C, active catalysts were detected when a gel was formed in the reaction mixture.

3.2. Typical polymerization of MMA

In a Schlenk tube under argon, 9.35 μ moles of metals and 18.7 μ mol of ligand were introduced with 100 μ L of THF. The solution was stirred 2 h at 30 °C. The solvent was eliminated by reduced pressure. 41 μ L of MAO solution (30% wt in toluene) were added and after 30 min at 30 °C, 2 mL of toluene was added. The MMA (1 mL, 9.35 mmol) was then added and the mixture was stirred 4 h at 30 °C. Finally, the polymerization experiment was stopped by pouring the content of the Schlenk tube in a large excess of methanol containing a small amount of hydrochloric acid. The coagulated polymer was washed with methanol, filtered and finally dried under vacuum. The polymer yield was determined by gravimetry.

3.3. Polymer characterization

Molecular weights and molecular weight distributions of the polymers were determined by size exclusion chromatography (SEC) at 40 °C in chloroform. A Dionex P680 HPLC pump equipped with the PL-ELS 1000 from Polymer Laboratories was used and connected to a PLgel 10 μ m MIXED-B column. PMMA standards were used for calibration (~1 mg/mL; injection volume 20 μ L; flow rate 1 mL/min). Differential scanning calorimetry (DSC) analy-

sis was performed on a TA-Instrument DSC2010. NMR spectra were recorded using Bruker Advance 300 MHz or Bruker DPX 200 MHz spectrometers. Chemical shifts are reported in δ (ppm) using CDCl₃ as the reference solvent unless otherwise stated. The triad tacticity of the polymers was determined by using the area ratios of the splitting α -methyl protons in the ¹H NMR spectra recorded at 300 MHz. HRMS were obtained with a VARIAN MAT311 and microanalysis with a Microanalyseur Flash EA1112 CHNS/O (Centre Régional de Mesures Physiques de l'Ouest, Rennes, France).

3.4. Synthesis of complex [CuCl₂] (**1b**)

CuCl₂ (110 mg, 0.82 mmol) and ligand **1b** (484 mg, 1.64 mmol) were dissolved in 10 mL of THF under stirring for 2 h at room temperature. THF was partially evaporated until the complex precipitated with 20 mL heptane. A green apple-like colored solid was filtered, washed twice with 20 mL heptane and dried under vacuum overnight. (348 mg, 99%). Anal. Calc. for C₁₈H₂₁Cl₂CuN₃O: C, 50.30; H, 4.92; N, 9.78. Found: C, 50.83; H, 5.54; N, 8.51%. Green crystals suitable for X-ray analysis were obtained from recrystallisation in THF-heptane (1:2, v/v). Crystal data: C₁₈H₂₁Cl₂CuN₃O; *M*_w 429.82; crystal size: 0.25 × 0.15 × 0.1 mm; temperature 100(2) K; wavelength 0.71073 Å; crystal system: monoclinic; space group: C2/c; unit cell dimensions: *a* = 22.1397(7) Å; *b* = 13.4559(4) Å; *c* = 14.5198(4) Å, α = 90°; β = 90.556(2)°; γ = 90°; *V* = 4325.4(2) Å³; *Z* = 8; *D*_c = 1.320 Mg/m³; absorption coefficient: 1.266 mm⁻¹; *F*(000) = 1768; θ -range for data collection: 3.03–27.48°; reflections collected/unique: 38485/4935 [*R*(int) = 0.0298]; limiting indices: $-28 \leq h \leq 28$, $-17 \leq k \leq 17$, $-18 \leq l \leq 18$; completeness to $\theta = 27.48$ (99.5%); max. and min. transmission: 0.881 and 0.715; data/restraints/parameters: 4935/0/226; goodness-of-fit on *F*² = 1.112; final *R* indices [*I* > 2 σ (*I*): *R*₁ = 0.0584, *wR*₂ = 0.1532; *R* indices (all data): *R*₁ = 0.0624, *wR*₂ = 0.1553; largest diffraction peak and hole: 1.362 and $-1.074 \text{ e \AA}^{-3}$.

3.5. Synthesis of complex [Cu(OAc)₂] (**1b**)

Cu(OAc)₂ · 6H₂O (200 mg, 1.00 mmol) was first dehydrated under vacuum at 90 °C overnight and then dissolved in 10 mL of THF with ligand **1b** (591.6 mg, 2.00 mmol) under stirring for 2 h at room temperature. THF was partially evaporated until the complex precipitated with 20 mL heptane. The blue solid was filtered, washed twice with 20 mL heptane and dried under vacuum one night (180 mg, 37%). Blue crystals were obtained from recrystallisation in THF-heptane (1:2, v/v). Crystal data: C₂₂H₂₇CuN₃O₅; *M*_w 477.01; crystal size: 0.3 × 0.15 × 0.1 mm; temperature: 120(2) K; wavelength: 0.71069 Å; crystal system: triclinic; space group: P $\bar{1}$; unit cell dimensions: *a* = 8.397(5) Å; *b* = 11.074(5) Å; *c* = 13.132(5) Å; α = 100.469(5)°; β = 104.559(5)°; γ = 99.805(5)°; *V* =

1131.9(9) Å³; $Z = 2$; $D_c = 1.400 \text{ Mg/m}^3$; adsorption coefficient: 1.002 mm^{-1} ; $F(000) = 498$; θ -range for data collection: $2.57\text{--}27.44^\circ$; limiting indices: $-10 \leq h \leq 10$, $-14 \leq k \leq 14$, $-16 \leq l \leq 17$; reflections/collected/unique: 9274/5131 [$R(\text{int})=0.0491$]; completeness to $\theta = 27.44$ (99.3%); data/restraints/parameters: 5131/0/280; goodness-of-fit on F^2 : 1.056; final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0610$, $wR_2 = 0.159$; R indices (all data) $R_1 = 0.0735$, $wR_2 = 0.1695$; largest diffraction peak and hole: 1.359 and $-1.350 \text{ e \AA}^{-3}$.

4. Supplementary material

CCDC 658502 and 658503 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.

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