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Reactivity of bulky tris(phenylpyrazolyl)methanesulfonate copper(I) complexes towards small unsaturated molecules

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ABSTRACT

Reaction of the tris(3-phenylpyrazolyl)methane sulfonate species ($Tpms^{Ph}$)Li with the copper(I) complex $[Cu(MeCN)_4][PF_6]$ affords [Cu($Tpms^{Ph}$)(MeCN)] **1**. The latter, upon reaction with equimolar amounts of cyclohexyl- (CyNC) or 2,6-dimethylphenyl (XylNC) isocyanides, or excess CO, furnishes the corresponding Cu(I) complexes [Cu($Tpms^{Ph}$)(CNR)] (R = Cy **2**, Xyl **3**) or [Cu($Tpms^{Ph}$)(CO)] **4**. The ligated isocyanide in **2** or **3** (or the acetonitrile ligand in **1**) is displaced by 3-iminoisoindolin-1-one to afford **5**, the first copper(I) complex containing an 3-iminoisoindolin-1-one ligand. The ligated acetonitrile in **1** undergoes nucleophilic attack by methylamine to give the amidine complex [Cu($Tpms^{Ph}$){MeC(NH)NHMe}] **6**, whereas only the starting materials were recovered from the attempted corresponding reactions of **2** and **3** with methylamine. Complexes **1** or **6** form the trinuclear hydroxo-copper(II) species [(μ-Cu){Cu(μ-OH)$_2$($Tpms^{Ph}$)}$_2$] **7** upon air oxidation in moist methanol. In all the complexes the scorpionate ligand facially caps the metal in the *N,N,O*-coordination mode.

1. Introduction

Copper complexes play a crucial role in different fields of science, *e.g.* in catalysis, coordination, bioinorganic and supramolecular chemistry, and, in particular, the use of poly(pyrazolyl) copper scaffolds to mimic enzymatic metal centres is well documented [1–7].

Within our studies on the coordination chemistry of *N*- and *O*-donor ligands [7–26], namely embracing the tris(pyrazolyl) methane scorpionate-type species [9–24], we have recently reported [12] the preparation of [Cu($Tpms^{Ph}$)(MeCN)] (**1**, Fig. 1), a new type of copper complexes bearing the sterically hindered chelating tris(3-phenylpyrazolyl)methane sulfonate ($Tpms^{Ph}$)$^-$ [27–29]. Now, we wish to further explore the steric and electronic features of this tripodal ligand (which is comparable to cyclopentadienyl on electronic and coordination grounds) for modulating the coordination properties of the metal centre, by testing the potential use of the nitrile complex **1** as a starting material for the syntheses of new complexes bearing the {Cu($Tpms^{Ph}$)} core as a convenient binding coordination site for various small molecules. This study was also encouraged by our continued interest on the activation of small unsaturated molecules upon coordination to late transition metals, *e.g.* isocyanides [30–39], nitriles [40–54], imines [30,31,42,55–58], and alkynes [59–62], among others.

2. Experimental section

2.1. General materials and experimental procedures

Syntheses were carried out under an atmosphere of dinitrogen, unless stated otherwise. Solvents were distilled prior to use. The reagents $[Cu(MeCN)_4][PF_6]$, cyclohexyl (CyNC) and 2,6-dimethylphenyl (XylNC) isocyanides (Aldrich) were purchased and used without further purification. ($Tpms^{Ph}$)Li, [Cu($Tpms^{Ph}$)(MeCN)] (**1**) [12] and 3-iminoisoindolin-1-one [58] were synthesised in accord to the literature methods. C, H and N analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Infrared spectra (4000–400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets and far infrared spectra (400-200 cm^{-1}) were recorded on a Vertex 70 spectrophotometer, in polyethylene and cesium iodide pellets. Vibrational frequencies are expressed in cm^{-1}; abbreviations: s, m

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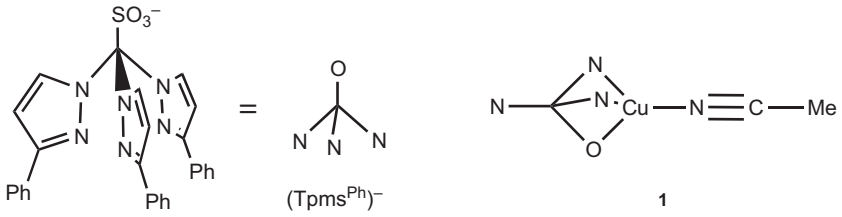


Fig. 1. Sterically hindered tris(3-phenylpyrazolyl)methane sulfonate $(Tpms^{Ph})^-$ and the corresponding acetonitrile copper(I) chelate **1**.

and w: strong, medium and weak, respectively. ^{1}H, ^{13}C{^{1}H} and ^{1}H, ^{1}H-COSY NMR experiments were acquired on Bruker 300 and 400 UltraShield™ spectrometers. ^{1}H and ^{13}C chemical shifts δ are expressed in ppm relative to $Si(Me)_4$. Coupling constants are in Hz; abbreviations: s, singlet; d, doublet; m, complex multiplet; vt, virtual triplet; br, broad. ESI$^+$ mass spectra were obtained on a VARIAN 500-MS LC ion trap mass spectrometer (solvent: methanol; flow: 20 μL/min; needle spray voltage: ±5 kV, capillarity voltage: ±100 V; nebulizer gas (N_2): 35 psi; drying gas (N_2): 10 psi; drying gas temperature: 350 °C).

2.1.1. [Cu(Tpms^{Ph})(CyNC)] (**2**)

To a methanolic solution (50 mL) of $[Cu(MeCN)_4][PF_6]$ (0.320 g, 0.86 mmol, 1 equiv) were added 3 mL of a Li(Tpms^{Ph}) solution (0.450 g, 0.85 mmol, 1 equiv) in the same solvent. The colourless solution was stirred for 5 min at room temperature with precipitation of [Cu(Tpms^{Ph})(MeCN)] (**1**). The suspension was then stirred for 15 min and cyclohexyl isocyanide (110 μL, 0.89 mmol, 1.1 equiv) was slowly added portionwise and the stirring of the reaction mixture was continued overnight at 20–25 °C. The formed white powder of **2** was collected by filtration, washed with cold methanol (2 × 25 mL), then recrystallized from cold acetone at 5 °C (0.740 g, 88%). Complex **2** is well soluble in medium polarity solvents such as Me_2CO, $CHCl_3$ and CH_2Cl_2, less soluble in H_2O ($S_{25°C} \approx 3$ mg mL^{-1}), MeOH, EtOH or DMSO and insoluble in C_6H_6 and Et_2O. **2**, $C_{35}H_{32}N_7SO_3Cu$ (694.29): calcd. C 60.55, N 14.12, H 4.64, S 4.61; found C 61.03, N 14.09, H 4.80, S 4.34. ESI$^+$-MS: 694 [M]$^+$. IR (KBr): 3150 (w), 2935 (m, ν(C–H)), 2860 (w, ν(C–H)), 2191 (s, ν(CN)), 1535 (m, ν(C=N)), 1500 (m), 1458 (m), 1358 (m), 1274 (s), 1235 (s), 1042 (s, ν(S–O)), 1059 (m), 856 (w), 758 (s), 641 (s, ν(C–S)), 534 (w) cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$, 298 K): 8.20–7.66 (m br, 3H + 6H, 5H (pz) + *o*-H (Ph)), 7.46–7.39 (m br, 9H, *m*,*p*-H (Ph)), 6.69 (d, 3H, J_{HH} = 2.7 Hz, 4-H (pz)), 3.38 (m, 1H, C*H*(Cy)), 1.50–1.27 (m, 10H, $(CH_2)_5$ (Cy)). ^{1}H NMR (300.130 MHz, $CDCl_3$, 213 K): 9.04 (s br, 1H, 5-H (pz)), 7.85 (m br, 6H, *o*-H (Ph)), 7.47 (m br, 9H, *m*,*p*-H (Ph)), 7.02 (s br, 2H, 5-H (pz)), 6.96 (s br, 1H, 4-H (pz)), 6.66 (s br, 2H, 4-H (pz)), 3.16 (m, 1H, C*H*(Cy)), 1.81–1.12 (m br, 10H, $(CH_2)_5$(Cy)). X-ray quality single crystals were grown by slow diffusion of dry diethyl ether in a concentrated solution of the titled compound in dichloromethane, under dinitrogen atmosphere.

2.1.2. [Cu(Tpms^{Ph})(XylNC)] (**3**)

To a methanolic suspension (50 mL) of [Cu(Tpms^{Ph})(MeCN)] (**1**, 0.200 g, 0.32 mmol, 1 equiv), 2,6-dimethylphenyl isocyanide (0.046 g, 0.35 mmol, 1.1 equiv) was added portionwise. The milky mixture was stirred at room temperature overnight under a dinitrogen atmosphere. The formed white powder of **3** was collected by filtration, washed with cold methanol (2 × 25 mL) and dried (0.180 g, 78%). Complex **3** is well soluble in medium polarity solvents such as Me_2CO, $CHCl_3$ and CH_2Cl_2, less soluble in H_2O ($S_{25°C} \approx 3$ mg mL^{-1}), MeOH or EtOH, and insoluble in Et_2O. **3**, $C_{37}H_{30}N_7O_3SCu$ (716.30): calcd. C 62.04, N 13.69, H 4.22, S 4.47; found C 62.43, N 13.13, H 4.43, S 4.14. ESI$^+$-MS: 716 [M]$^+$. IR (KBr): 3142 (w), 3059 (m, ν(C–H)), 2922 (m, ν(C–H)), 2153 (s, ν(CN)), 1535 (m, ν(C=N)), 1500 (m), 1459 (m), 1375 (m), 1280 (s), 1236 (s), 1043 (s, ν(S–O)), 858 (w), 757 (s), 630 (s, ν(C–S)), 539 (w) cm^{-1}. ^{1}H NMR (300.130 MHz, $CDCl_3$, 298 K): 7.82 (d, 6H, J_{HH} = 7.5 Hz, *o*-H (Ph)), 7.76 (d, 1H, J_{HH} = 8.0 Hz, *p*-H(XyNC)), 7.70 (d, 1H, J_{HH} = 2.5 Hz, 5-H (pz)), 7.46–7.29 (m br, 9H + 2H, *m*-H(XyNC) + *m*,*p*-H (Ph)), 7.19 (d, 2H, J_{HH} = 2.5 Hz, 5-H (pz)), 6.67 (m br, 3H, 4-H (pz)), 2.17 (s, 6H, Me from (XyNC)).

2.1.3. [Cu(Tpms^{Ph})(CO)] (**4**)

3 mL of a methanolic solution of Li(Tpms^{Ph}) (0.042 g, 0.081 mmol, 1 equiv) were added to a solution (10 mL) of $[Cu(MeCN)_4][PF_6]$ (0.030 g, 0.081 mmol, 1 equiv) in the same solvent contained in a stainless steel vessel. The final solution, with the *in situ* generated acetonitrile complex **1**, was saturated with pressurized carbon monoxide (20 atm) and stirred at room temperature overnight. Then the solvent was removed under vacuum and the solid washed with cold methanol (5 mL) and dried to afford **4** as a white powder (0.034 g, 68%). Complex **4** is soluble in Me_2CO, $CHCl_3$ and CH_2Cl_2, less soluble in H_2O ($S_{25°C} \approx 3$ mg mL^{-1}), MeOH or EtOH and insoluble in Et_2O. **4**, $C_{29}H_{21}N_6O_4SCu$ (613.13): calcd. C 56.81, H 3.45, N 13.71, S 5.23; found C 56.88, H 3.54, N 13.41, S 5.33. ESI$^+$-MS: 613 [M]. IR (KBr): 3158, 3125 (w), 2960, 2935 (m), 2860 (w), 2107 (m, ν(CO)), 1535 (m, ν(C=N)), 1500 (m), 1459 (m), 1356 (m), 1271 (s), 1237 (s), 1078 (s, ν(S–O)), 1044 (m), 867 (w), 758 (s), 639 (s, ν(C–S)), 540 (w) cm^{-1}. ^{1}H NMR (300.130 MHz, $CDCl_3$, 298 K): 8.02 (s br, 3H, 5-H (pz)), 7.94 (d, 6H, J_{HH} = 7.5 Hz, *o*-H (Ph)), 7.49–7.44 (m br, 9H, *m*,*p*-H (Ph)), 6.96 (d, 3H, J_{HH} = 2.6 Hz, 4-H (pz)).

2.1.4. [Cu(Tpms^{Ph})(3-iminoisoindolin-1-one)] (**5**)

Solid 3-iminoisoindolin-1-one (0.008 g, 0.05 mmol, 1 equiv) was added to a chloroform solution (10 mL) of [Cu(Tpms^{Ph})(XylNC)] (**3**) (0.036 g, 0.05 mmol, 1 equiv). The resulting orange suspension was refluxed overnight under dinitrogen, leading to a bright-yellow solution. The latter was left to stand at room temperature for *ca.* 1 h, filtered to remove some insoluble materials, and the filtrate was evaporated to dryness forming a yellowish-orange powder which was washed with cold diethyl ether (3 × 5 mL) and dried under vacuum at 20–25 °C to afford **5** (0.031 g, 84% yield). Reaction of **1** or **2** with 3-iminoisoindolin-1-one proceeds under similar conditions furnishing **5** in 81 or 82% yields, respectively. Complex **5** is well soluble in medium polar solvents such as Me_2CO, $CHCl_3$ and CH_2Cl_2, and insoluble in Et_2O. **5**, $C_{36}H_{26}N_8O_4SCu$ (730.25): calcd. C 59.21, H 3.59, N 15.34, S 4.39; found C 59.60, H 3.52, N 15.18, S 4.43. ESI$^+$-MS: 730 [M + H]. IR (KBr): 3236 w-m ν(N–H), 3140 (w), 3097 (w), 3067 (w), 2922 (m), 1728 (m), 1691 (m), 1624 (s) ν(C=O) and ν(C=N), 1562 (m) δ(N–H), 1455 (m), 1383 (m), 1230 (s), 1043 (s) ν(S–O), 858 (w), 758 (s), 637 (s) ν(C–S) cm^{-1}. ^{1}H NMR (400.130 MHz, $CDCl_3$, 298 K): 8.20 (s, br, 1H, NH), 7.86–7.83 (m, 6H + 3H, *o*-H (Ph) + 5-H (pz)), 7.74–7.41 (m, 4H + 6H + 3H, 3-iminoisoindolin-1-one + *m*-H (Ph) + *p*-H (Ph)), 6.69 (m br, 3H, 4-H (pz)). ^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$, 298 K): 155.1 (C=O),

154.6 (s, 3-C (pz)), 136.8 (br, C=N), 135.8 (s, 5-C (pz)), *ca.* 133.5 (br, 3-iminoisoindolin-1-one(Ph)), 131.7 (s, pz-*C* (Ph)), *ca.* 130.5 (br, 3-iminoisoindolin-1-one(Ph)), 129.0 (s, *p*-C (Ph)), 128.4 (s, *m*-C (Ph)), 127.6 (s, *o*-C (Ph)), 105.4 (s, 4-C (pz)), 98.0 (br, O_3SC).

*2.1.5. [Cu(Tpms^{Ph}){MeC(=NH)NHMe}] (**6**)*

To a dichloromethane solution (3 mL) of [Cu(Tpms^{Ph})(MeCN)] (**1**) (0.040 g, 0.064 mmol, 1 equiv) was added a 2.0 M THF solution of monomethylamine (32 μL, 0.064 mmol, 1 equiv). The resulting colourless solution was stirred at room temperature for 3 h under dinitrogen. The solvent was removed under vacuum and the residue was washed with cold methanol (5 mL) and dried to afford **6** (0.026 g, 61%). Complex **6** is well soluble in medium polarity solvents such as Me_2CO, $CHCl_3$ or CH_2Cl_2, less soluble in H_2O ($S_{25°C} \approx 4$ mg mL^{-1}), MeOH or EtOH, and insoluble in Et_2O. **6**, $C_{31}H_{29}N_8O_3SCu$ (657.23): calcd. C 56.65, N 17.04, H 4.45, S 4.87; found C 57.10, N 16.98, H 4.67, S 4.62. ESI$^+$-MS: 657 [M]. IR (KBr): 3323, 3276 (m, ν(NH)), 3127 (w), 3059 (m), 1604, 1532 (m, ν(C=N)), 1499 (m), 1458 (m), 1372 (m), 1268 (s), 1237 (s), 1104, 1078, 1044 (s, ν(S–O)), 854 (w), 697 (s, ν(C–S)), 539 (w) cm^{-1}. ^{1}H NMR (400.130 MHz, $CDCl_3$, 298 K): 7.87 (m br, 6H + 3H, 5-H (pz) + *o*-H (Ph)), 7.43 (m br, 9H, *m*,*p*-H (Ph)), 6.71 (s br, 3H, 4-H (pz)), 3.75 (s b, 1H, N*H*-Me) 2.17 (s, 3H, Me-C), 1.85 (s br, 3H, *Me*-NH); ^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$-d_6, 298 K): 157.2 (s br, Cu–N=*C*), 154.0 (s, 3-C (pz)), 135.9 (s, 5-C (pz)), 131.9 (s, pz-C (Ph)), 129.1 (s, *p*-C (Ph)), 128.6 (s, *m*-C (Ph)), 127.1 (s, *o*-C (Ph)), 105.2 (s, 4-C (pz)), 96.0 (s, O_3SC), 2.3 (s, NH-Me), 1.8 (s, C*Me*).

*2.2. Attempted reaction of **2** or **3** with methylamine*

To a dichloromethane solution (3 mL) of [Cu(Tpms^{Ph})(RNC)] (**2** or **3**, 0.064 mmol, 1 equiv) was added a 2.0 M THF solution of monomethylamine (32 μL, 0.064 mmol, 1 equiv). The resulting colourless solution was refluxed for *ca.* 24 h under dinitrogen. The solvent was removed under vacuum and the residue was washed with cold methanol (5 mL) and dried. The obtained solid was analysed by IR, ^{1}H and ^{13}C NMR and ESI-MS indicating the presence of the starting **2** or **3**.

*2.2.1. [(μ-Cu){Cu(μ-OH)$_2$(Tpms^{Ph})}$_2$] (**7**)*

*2.2.1.1. Preparation from complex **6**.* A methanol/CH_2Cl_2 (3:1 v:v) solution (4 mL) of [Cu(Tpms^{Ph}){MeC(=NH)NHMe}] (**6**) (0.025 g, 0.038 mmol) was cooled down and kept, in air, in a fridge at *ca.* 4 °C overnight, thereafter the solution was decanted leaving a deep dark/green crystalline solid of **7** (22 mg, 44%). **7**, $C_{56}H_{46}N_{12}O_{10}S_2Cu_3$, (1301.81); calcd. C 51.66, N 12.91, H 3.56, S 4.93; found C 52.01, N 12.79, H 3.50, S 4.44. IR (KBr): 3430 (w, ν(O–H)), 3139 (w), 2964 (m), 1637 (w, δ (O–H)), 1535 (m, ν(C=N)), 1499 (m), 1457 (m), 1378 (m), 1261 (s), 1231 (s), 1079 (s), 1046 (s, ν(S–O)), 860 (w), 758 (s), 641 (s, ν(C–S)) cm^{-1}. X-ray quality single crystals were grown from a cooled concentrated solution of **7** in methanol/CH_2Cl_2 (3:1 v:v).

*2.2.1.2. Preparation from complex **1**.* To a methanolic solution (4 mL) of [Cu(Tpms^{Ph})(MeCN)] (**1**) (0.040 g, 0.064 mmol, 1 equiv), monomethylamine (32 μL, 0.064 mmol, 1 equiv) was added. The resulting colourless solution was stirred at room temperature for 3 h under dinitrogen. Then the system was open to air and CH_2Cl_2 (1 mL) was added to the reaction mixture which was further stirred for 1 h. The resulting green solution was cooled and kept, in air, in a fridge at *ca.* 4 °C overnight, to form a dark green powder of **7** (29 mg, 58%).

2.3. Crystal structure determination

Single crystals of **2** and **7** were obtained as indicated above. Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer with graphite monochromated Mo-Kα radiation. Data were collected at 150 K using omega scans of 0.5° per frame and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT [63] on all the observed reflections. Absorption corrections were applied using SADABS [64]. The structures were solved by direct methods by using the SHELXS-97 package [65] and refined with SHELXL-97 [66]. Calculations were performed using the WinGX System-Version 1.80.03 [67] and PLATON/SQUEEZE [68] was used to correct the data. Crystal data and refinement parameters are shown in Table 1.

3. Results and discussion

[Cu(Tpms^{Ph})(MeCN)] (**1**) was prepared according to a literature method by reaction of Li(Tpms^{Ph}) with [Cu(MeCN)$_4$][PF$_6$] [12]. It reacts with cyclohexyl isocyanide (CyNC) and 2,6-dimethylphenyl isocyanide (XylNC) in dry methanol leading to the formation of the corresponding isocyanide complexes [Cu(Tpms^{Ph})(CyNC)] (**2**) and [Cu(Tpms^{Ph})(XylNC)] (**3**), isolated as white solids in high yields (Scheme 1).

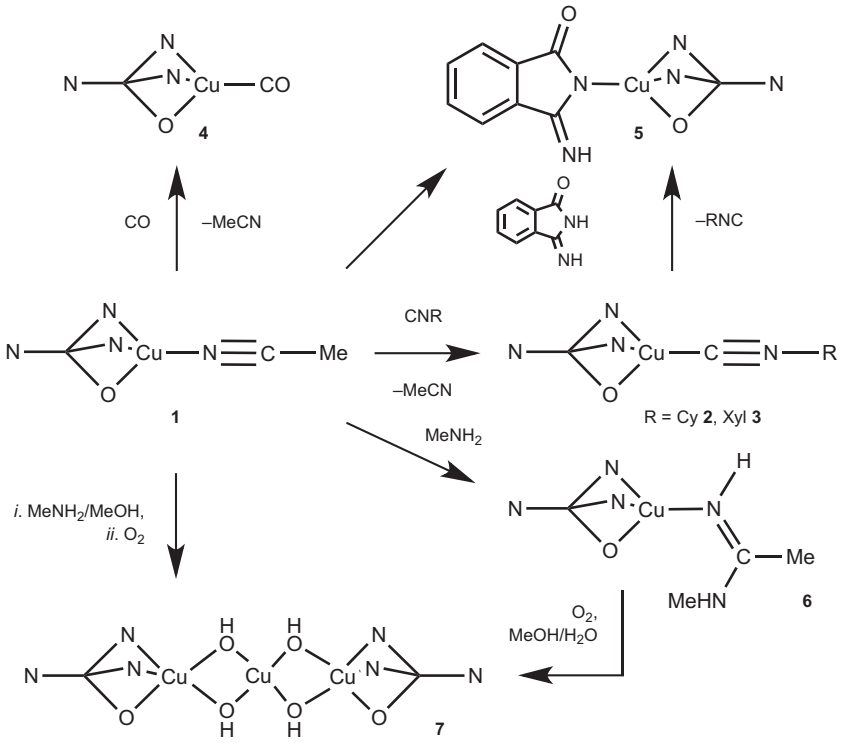
These products can also be obtained in a single-pot process, starting from the precursors of **1**, *i.e.*, [Cu(MeCN)$_4$][PF$_6$] and Li(Tpms^{Ph}). The acetonitrile complex **1** is then generated *in situ*, without isolation, and further reaction occurs with the appropriate isocyanide. Compounds **2** and **3** are moderately soluble in MeOH or EtOH, soluble in CH_2Cl_2 and $CHCl_3$, and sparingly soluble in water ($S_{25°C} \approx 3$ mg mL^{-1}). Their variable temperature ^{1}H NMR spectra indicate [12] that the scorpionate assumes the *N*,*N*,*O*-coordination mode which is retained in the solid state: their IR spectra display the ν_{SO} typical [29] of the coordinated sulfonate moiety (*i.e.* strong and sharp bands at 1042 and 1043 cm^{-1}). Compound **2** exhibits an X-ray crystal structure with the copper cation in an ON_2C environment (Fig. 2). Houser et al. [69] introduced a parameter (τ_4) to describe the geometry of a four-coordinate metal system which is determined by eq. (1), where α and β are the largest angles involving the metal.

$$\tau_4 = [360 - (\alpha + \beta)]/141° \quad (1)$$

By means of this simple criterion, perfect square planar, trigonal pyramid or tetrahedral geometries should have τ_4 values of 0, 0.85 or 1, respectively. In complex **2**, the τ_4 parameter has an intermediate value (0.65) and its geometry is better described as that of a seesaw. The Cu1–O1 bond length of 2.377(2) Å, even though long,

Table 1
Crystallographic data for compounds **2**·Et_2O and **7**.

	2·Et_2O	**7**
Crystal shape	Prism	Prism
Crystal colour	Colourless	Green
Empirical formula	$(C_{35}H_{32}CuN_7O_3S)_2 \cdot C_4H_{10}O$	$C_{56}H_{46}Cu_3N_{12}O_{10}S_2$
Formula weight	1462.67	1301.79
Crystal system	Monoclinic	Triclinic
Space group	*C*2/*c*	*P* − 1
a (Å)	27.422(2)	11.8151(11)
b (Å)	11.4315(7)	11.8270(11)
c (Å)	23.0916(17)	12.2171(10)
β	106.675(2)	107.437(4)
V (Å^3)	6934.2(8)	1578.2(2)
Z	4	1
ρ_{calc} (g cm^{-3})	1.401	1.370
μ (Mo-Kα) (mm^{-1})	0.740	1.130
F (000)	3048	2039
Refl. collected/unique	28,579/6331	14,950/5591
$R_1 = [I > 2\sigma(I)]$; *wR*2 (all data)	0.0464; 0.1093	0.0684; 0.1714
GOF	0.984	0.913



Scheme 1. Copper complexes bearing $Tpms^{Ph}$ ligands.

is within the sum of the corresponding van der Waals radii and is similar to those of the analogues [Cu($Tpms^{Ph}$)(MeCN)] (**1**) and [Cu($Tpms^{Ph}$)(HMT)] (HMT = hexamethylenetetramine) [12] and to the Cu–$O_{sulfonate}$ bond distances in complex **7** (see below).

Intense ν_{CN} stretching bands in the IR spectra of compounds **2** and **3** are seen at 2191 and 2153 cm^{-1}, respectively, values that are not markedly different from those of the corresponding uncoordinated isocyanides (*i.e.* 2135 and 2124 cm^{-1}, correspondingly), thus indicating that their activation upon coordination to the Cu centre should not be extensive [38,39]. Accordingly, the isocyanide ligand in **2** or **3** does not undergo attack by a nucleophile such as methylamine or 3-iminoisoindolin-1-one [31,42,56,58]. In fact, the unreacted starting compounds were isolated upon attempted reaction of **2** or **3** with methylamine, whereas isocyanide ligand displacement occurred with the iminoisoindolinone to give [Cu($Tpms^{Ph}$)(3-iminoisoindolin-1-one)] (**5**, Scheme 1). The same product can also be obtained upon direct reaction of the acetonitrile complex **1** with 3-iminoisoindolin-1-one. It is worthwhile to point out that examples of complexes containing ligated 3-iminoisoindolin-1-ones are scarce, and up to date were represented only by Pt(II) [31], Pd(II) [31] and Zn(II) [57] species, reported recently by some of us. Hence, within the current study, we succeed to extend such a type of complexes to copper(I).

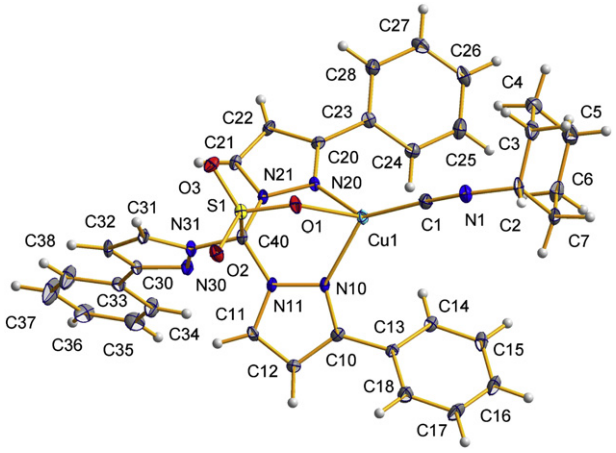


Fig. 2. Plot of [Cu($Tpms^{Ph}$)(CyNC)] (**2**), with ellipsoids shown at 30% probability (Et_2O molecule was omitted for clarity). Selected bond lengths [Å] and angles [°]: Cu1–N10 2.022(3); Cu1–N20 2.021(3); Cu1–O1 2.377(2); Cu1–C1 1.835(4); C1–N1 1.151(4); N1–C2 1.467(4); Cu1–C1–N1 177.1(3); C1–N1–C2 174.7(3); N20–Cu1–N10 87.96(10); C1–Cu1–O1 110.67(11); N20–Cu1–O1 86.61(9); N10–Cu1–O1 82.50(9).

Surprisingly, in contrast with the behaviour of the isocyanide complexes **2** and **3**, the reaction of the acetonitrile complex **1** with methylamine (a stronger protic nucleophile than the above iminoisoindolinone) led to the formation of the amidine product [Cu($Tpms^{Ph}$){MeC(=NH)NHMe}] (**6**) derived upon nucleophilic addition of the amine to the nitrile ligand (Scheme 1). Compound **6** was not successfully crystallized for X-ray analysis, but the ^1H NMR spectrum shows the characteristic resonances for the N_2O-coordination mode [12] that appears to be retained in solution from the starting material **1**. Moreover, the ^{13}C NMR spectrum of **6** displays the typical C=N carbon resonance at δ 157 ppm drastically shifted from the carbon resonance of the corresponding nitrile in **1** (*i.e.* δ 116.18) [12].

The acetonitrile displacement in **1** by carbon monoxide was also investigated. Many attempts under different conditions, viz. at various CO pressures (1–6 atm), reaction temperatures (from −78 °C to 40 °C) and different solvents (MeOH, CH_2Cl_2) within 6–72 h period, were unsuccessful, showing an unexpected difficulty to achieve the carbonyl analogue of **1**. Exclusively by using a relatively high CO pressure (20 atm) in a closed vessel containing acetonitrile solution of **1**, was possible to isolate from a methanol solution the expected carbonyl complex [Cu($Tpms^{Ph}$)(CO)] (**4**) after *ca.* 12 h. The observed difficulty in the preparation of **4**, in contrast

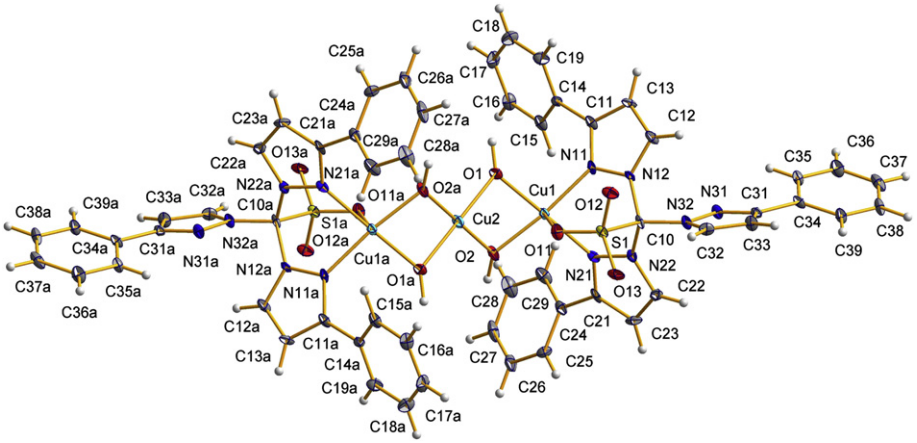


Fig. 3. Plot of [(μ-Cu){Cu(μ-OH)$_2$(Tpms^{Ph})}$_2$] (**7**), with ellipsoids shown at 30% probability. Hydrogen atoms were omitted for clarity. Symmetry codes to generate equivalent atoms: a) $-x, 1-y, 1-z$. Selected bond lengths [Å] and angles [°]: O1–Cu2 1.914(4); O1–Cu1 1.918(5); O2–Cu1 1.914(4); O2–Cu2 1.913(5); N11–Cu1 1.972(5); N21–Cu1 1.974(6); O11–Cu1 2.361(4); Cu1–Cu2 2.7902(8); Cu2–O1–Cu1 93.5(2); Cu2–O2–Cu1 93.6(2); O2–Cu1–O1 79.5(2); O2–Cu1–N11 173.5(2); O1–Cu1–N11 94.9(2); O2–Cu1–N21 99.9(2); O1–Cu1–N21 176.8(2); N11–Cu1–N21 85.9(2); O2–Cu1–O11 95.00(19); O1–Cu1–O11 91.32(19); N11–Cu1–O11 88.33(19); N21–Cu1–O11 85.60(19).

to the case of related complexes with a comparable scorpionate ligand but without the sulfonate group [70–72], could suggest an eventual role of this group. Complex **4** shows ν_{CO} at 2107 cm^{-1}, consistent with those of the related Cu(I) complex [Cu(Tpm^{Ph})(CO)][PF$_6$]) [70], bearing the neutral tris(phenylpyrazolyl)methane, and similar compounds of tris(pyrazolyl)borate and tris(pyrazolyl) methane [71], and suggesting [72] the retention of the N$_2$O-coordination mode of the scorpionate in **4**.

Furthermore, although the bulkiness of the {Cu-Tpms^{Ph}} moiety prevents the formation of full sandwich complexes with two Tpms^{Ph} ligands, a polynuclear compound can be formed bearing such a group at a terminal position. In fact, the trinuclear complex [(μ-Cu){Cu(μ-OH)$_2$(Tpms^{Ph})}$_2$] (**7**) was isolated from a cooled solution of **6** in methanol/CH_2Cl_2 left in air. The latter species can also be obtained directly from **1**, via a single pot procedure, in methanol with $MeNH_2$ followed by exposure to air (Scheme 1). The formulation of **7** is based on data of elemental analyses, IR spectroscopy, and single crystal X-ray diffraction. As it can be inferred from the inspection of the plot of the molecular structure of **7** (Fig. 3), Cu1 is the case of a five-coordinate metal system, for which Addison and Reedijk proposed [73] the τ_5 parameter to describe the metal geometry determined by eq. (2), where β and α are the largest angles involving the metal; therefore, τ_5 may assume values of 0 or 1 for perfect square pyramid or trigonal bipyramid geometries, respectively

$$\tau_5 = [(\beta - \alpha)]/60^\circ \quad (2)$$

According to this criterion, the O_3N_2 copper environment in **7** features an almost perfect square pyramid ($\tau_5 = 0.06$). The Cu2 metal cation, being located in an inversion centre, presents a perfect square planar geometry ($\tau_4 = 0$). In **7** the Cu–O bond distances average 1.915(5) Å while the Cu–O$_{sulphonate}$ length is, unsurprisingly (see above), considerably longer (2.361(4) Å).

The geometries of the complexes (seesaw in **2** and square pyramid for Cu1 in **7**) have an influence on several structural parameters. For example, the Cu1 cation in **2** is 0.815 Å above the plane defined by the N atoms of the coordinated pyrazolyl rings; in **7** that distance is of 0.917 Å. Moreover, the N–Cu–N bond angle in **2** [87.96(10)°] is wider than those in **7** [85.9(2)°] while the N–Cu–O$_{sulfonate}$ angles are narrower in the former [*av.* 84.55(9)°] relative to the latter [*av.* 86.97(19)°]; consequently, the Cu1···C$_{quaternary}$ distance in **2** is longer than that in **7** (3.188 and 3.170 Å, respectively). The shortest intramolecular Cu···Cu bond distance in **7** is of 2.7902(8) Å.

4. Conclusions

The {copper (I)–Tpms^{Ph}} moiety provides a reactive scaffold for small coordinating molecules (such as, nitriles, isocyanides and CO) leading to a series of κ^3–Tpms^{Ph}–Cu complexes bearing the coordinated sulfonate arm. These products represent a potential class of catalysts with a flexible labile ligand that may provide convenient entries to further reactivity studies [74–77].

The metal-activation of the CN triple bond in the Cu^I compounds is limited [38,39,50], but could be successfully exploited in the case of a small and sufficiently strong nucleophile, such as methylamine, that leads to the formation of the product of nucleophilic addition to a ligated acetonitrile, *i.e.* an acetamidine complex, whereas the bulkier 3-iminoisoindolin-1-one nucleophile displaces the labile acetonitrile or isocyanide ligands affording the first copper complex with such a ligand, *i.e.*, [Cu(Tpms^{Ph})(3-iminoisoindolin-1-one)] (**5**).

Moreover, the formation of the extended tricopper core in complex **7** provides a promising starting point for the design of multi-copper(II) biomimetic models, what deserves to be further explored.

These examples emphasize the important role of the bulky scorpionate (Tpms^{Ph})$^-$ which acts as a steric but flexible shield modulating the coordination chemistry of the Cu centre towards small molecules, namely those indicated above.

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Appendix A. Supplementary material

CCDC numbers 818625 and 818629 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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