Reactivity of homoleptic and heteroleptic core paddle wheel Cu(II) compounds

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Abstract

The compound $[\text{Cu}(\mu\text{-Pip})(\mu\text{-OAc})(\text{MeOH})]_2$ (**1**) (Pip = Piperonylate, OAc = acetate, MeOH = methanol) has been obtained in a high percentage yields. Its reactivity with pyridine/pyrazole derivative ligands (pyridine (py), 3-phenylpyridine (3-Phpy) and 4-acetylpyridine (4-Acpy)) and 3,5-dimethylpyrazole (3,5-dmpz) leads to four monomeric compounds: $[\text{Cu}(\text{Pip})_2(\text{dPy})_2(\text{H}_2\text{O})]$ (dPy= py (**2**), 3-Phpy (**3**) and 4-Acpy (**4a**)) and $[\text{Cu}(\text{Pip})_2(3,5\text{-dmpz})_2]$ (**5**). Furthermore, the reaction of **1** with HPip in MeOH:DMF solvent under reflux conditions yields the homoleptic core paddle-wheel compound $[\text{Cu}(\mu\text{-Pip})_2(\text{DMF})]_2 \cdot 2\text{DMF}$ (**6**). In the reaction between **6** and 2-benzylpyridine (2-Bzpy) yields the paddle-wheel core compound $[\text{Cu}(\text{Pip})_2(2\text{-Bzpy})]_2$ (**7**). All compounds have been fully characterized by analytical and spectroscopic techniques and their X-ray crystal structures have been determined. In this set of compounds, the carboxylate ligand (Pip) displays different coordination modes (monodentate (**2-4**), bidentate chelate (**5**) and bridged (**1**, **6** and **7**)). Moreover, their supramolecular network is discussed: the crystal packing indicates hydrogen bond propagation defines 1D (**2-5**) or 2D (**6** and **7**) supramolecular networks.

1. Introduction

The synthesis and characterization of crystalline materials build up by covalent bonds has gained an important interest, specially, the association of molecular compounds to form extended solids starting from secondary building units (SBUs) [1,2]. The assembly of metal-carboxylates for constructing new SBUs is an extensively exploited research field. These kind of compounds play an important role in synthetic chemistry, thanks to their labile coordination mode and even more important, in the design of porous frameworks [3].

Supramolecular chemistry is also an emergent research area, providing new complexes, which form chemical systems different from those linked with covalent bonds. These systems are composed of two or more assembled molecular subunits joined by relatively weak intermolecular forces (hydrogen bond, hydrophobic and π -interactions, van der Waals forces, and electrostatic effects) [1,4].

An important family of SBUs are Cu(II) and Zn (II) paddle-wheel complexes. There are more than 1,400 crystal structures containing Cu(II) with a $[\text{Cu}_2\text{L}_4]$ ($\text{L}=\text{R}-\text{COO}$) homoleptic *core* [5]. From those, only twelve present mixed bridged carboxylates $[\text{Cu}(\text{L})(\text{L}')(\text{X})]_2$ [6-16] in which six structures are accomplished via acetate bridging units [8-11, 13, 14]. There is not a rigorous explanation for its formation; steric hindrance could only play a significant role in three of them [11, 13]. Recently, we have been studying the role of carboxylic acids in the structural arrangement. In this sense, reactions with 4-hydroxybenzoic acid (HpOHBz), (E)-3-(4-hydroxyphenyl)-2-propenoic acid (para-hydroxycinnamic acid, HpOHcinn) and 1,3-benzodioxole-5-carboxylic acid (Piperonylic acid, HPip) with Cu(II) [17-20], Zn(II) [21] and Cd(II) [21] have been already studied.

Herein, we focus on this novel compound with an heteroleptic paddle-wheel *core* $[\text{Cu}(\mu\text{-Pip})(\mu\text{-OAc})(\text{MeOH})]_2$ (**1**) (OAc = acetate), recently obtained in our research group [18]. Homoleptic *core* paddle-wheel have been vastly used as starting building units for design of supramolecular [6] or polymeric [22] architectures while there is not any research with those

containing a heteroleptic paddle-wheel core. Herewith, the reactivity of **1** with pyridine/pyrazole derivative ligands (pyridine (py, **2**); 3-phenylpyridine (3-Phpy, **3**); 4-acetylpyridine (4-Acpy, **4**) and 3,5-dimethylpyrazole (3,5-dmpz, **5**)) have been studied, resulting in monomeric compounds $[\text{Cu}(\text{Pip})_2(\text{dPy})_2(\text{H}_2\text{O})]$ (**2-5**). The displacement of the two remaining acetate units of **1** allow us to reach the homoleptic paddle-wheel $[\text{Cu}(\text{Pip})_2(\text{DMF})]_2 \cdot 2\text{DMF}$ (**6**) and gives us the possibility to perform further reactivity with 2-benzylpyridine ligand (2-Bzpy), which yields $[\text{Cu}(\text{Pip})_2(2\text{-Bzpy})]_2$ (**7**) (Scheme 1).

2. Experimental Section

2.1. Materials and methods

Cu(II) acetate monohydrate ($\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$), 1,3-benzodioxole-5-carboxylic acid (piperonylic acid, HPip), pyridine (py), 3-phenylpyridine (3-Phpy), 4-acetylpyridine (4-Acpy), 2-benzylpyridine (2-Bzpy) and 3,5-dimethylpyrazole (3,5-dmpz) ligands; methanol (MeOH), *N,N*-dimethylformamide (DMF) and hexane were used as solvents. All of them were purchased from Sigma-Aldrich and used without further purification. Reactions and manipulation were carried out in air at room temperature (r.t.) for compounds **1-3** and under reflux conditions for **4-7**. Elemental analysis (C, H, N) were carried out on a Thermo Scientific Flash 2000 CHNS Analyzer. The ATR-FTIR spectra were recorded on a Perkin Elmer spectrometer, equipped with a universal attenuated total reflectance (ATR) accessory with diamond window in the range 4000-550 cm^{-1} . The electronic spectra in solution of MeOH ($\approx 1 \cdot 10^{-3}$ M) were run on a spectrophotometer Cary 500 Varian, equipped with a quartz cell having a path length of 1 cm in the range of 500-800 nm. Powder X-ray diffraction (PXRD) patterns were measured with a Siemens D5000 apparatus (with 40 kW and 45 mA using $\text{CuK}\alpha$ radiation with $\lambda = 1.5406 \text{ \AA}$). All of them were recorded from $2\theta = 5^\circ$ to 30° with a step scan of 0.02° counting 1s at each step.

[Insert Scheme 1]

2.2. Synthetic procedures

2.2.1. $[Cu(\mu\text{-Pip})(\mu\text{-OAc})(\text{MeOH})]_2$ (**1**)

To a solution containing HPip (503 mg, 3.03 mmol) in MeOH (120 mL), the green powder $Cu(OAc)_2 \cdot H_2O$ (550 mg, 3.03 mmol) was added portion wise and stirred for 5 h at r.t, a green precipitate appeared immediately. The product was filtered off, washed with 10 mL of cold methanol and dried on air. Yield: 865 mg (89%). The same reaction was also performed in presence of AcOH acid (3.0 mL) with similar yield (845 mg, 87%) (S.I.: Fig. S1). Elem. Anal. Calc. for $C_{22}H_{24}O_{14}Cu_2$ (639.52 g/mol): C 41.32; H 3.78. Found: C 41.05; H 3.54%. ATR-FTIR (wavenumber, cm^{-1}): 3301(m) $[v(O-H)]_{MeOH}$, 3060(w) $[v_{ar}(C-H)]$, 2955(w) $[v_{al}(C-H)]$, 1628(m), 1593(s) $[v_{as}(COO)]$, 1508(w) $[v_{ar}(C=C)]$, 1493(m), 1442(s) $[v_s(COO)]$, 1390(s), 1356(m), 1265(s) $[\delta(OH)]$, 1244(m), 1174(w), 1117(m) $[v(C-O-C)]$, 1079(w), 1036(m), 1022(s) $[\delta_{ip}(C-H)]$, 935(w), 922(m), 884(w), 804(m), 775(s) $[\delta_{oop}(C-H)]$, 684(s) $[\delta_{oop}(C-H)]$, 628(m). UV-Vis (Methanol, $1.1 \cdot 10^{-3}$ M) λ_{max} (ϵ) = 716 (124) nm.

2.2.2. $[Cu(Pip)_2(py)_2(H_2O)]$ (**2**)

To a solution containing **1** (100 mg, 0.156 mmol) in MeOH (40 mL), a solution of py (0.25 mL, 3.13 mmol) in MeOH (10 mL) was added dropwise and stirred for 1 h. The solution turned dark blue and was subjected to several cooling-evaporation cycles. The resulting blue powder was filtered off, washed with 10 mL of cold methanol and dried on air. Suitable blue crystals were obtained after evaporation of mother liquors on air for 10 days. Yield: 55.2 mg (62%). Elem. Anal. Calc. for $C_{26}H_{22}N_2O_9Cu$ (569.99 g/mol): C 54.78; H 3.89; N 4.91. Found: C 54.92; H 3.75; N 4.84%. ATR-FTIR (wavenumber, cm^{-1}): 3291(w) $[v(O-H)]_{water}$, 3071(w) $[v_{ar}(C-H)]$, 2909(w) $[v_{al}(C-H)]$, 1607(m), 1579(s) $[v_{as}(COO)]$, 1566(s), 1501(m), 1487(m), 1448(m), 1434(s) $[v_s(COO)]$, 1379(s), 1346(s), 1255(s), 1239(s), 1220(m) $[\delta(OH)]$, 1166(m), 1109(m) $[v(C-O-C)]$, 1073(m), 1035(s) $[\delta_{ip}(C-H)]$,

934(m), 918(m), 802(m), 770(vs) [$\delta_{\text{oop}}(\text{C-H})$], 722(m), 705(s), 696(s), 678(s), 635(s), 607(s), 583(s). UV-Vis (Methanol, $9.7 \cdot 10^{-4}$ M) λ_{max} (ϵ) = 710 (33) nm.

2.2.3. $[\text{Cu}(\text{Pip})_2(3\text{-Phpy})_2(\text{H}_2\text{O})]$ (**3**)

To a solution containing 3-Phpy (226 mg, 0.313 mmol) in MeOH (10 mL), a green solution of **1** (100 mg, 0.156 mmol) in MeOH (30 mL) was added dropwise and stirred for 1 h. The solution turned dark blue and was treated as **2**. Suitable blue crystals were obtained after evaporation of the mother liquors on air for 20 days. Yield: 63.3 mg (56%). Elem. Anal. Calc. for $\text{C}_{38}\text{H}_{30}\text{N}_2\text{O}_9\text{Cu}$ (722.18 g/mol): C 63.20; H 3.19; N 3.88. Found: C 63.05; H 3.25; N 3.72%. ATR-FTIR (wavenumber, cm^{-1}): 3241(br) [$\nu(\text{O-H})$]_{water}, 3085(w) [$\nu_{\text{ar}}(\text{C-H})$], 2919(w) [$\nu_{\text{al}}(\text{C-H})$], 1569(s) [$\nu_{\text{as}}(\text{COO})$], 1500(w), 1476(w), 1439(s), 1362(s) [$\nu_{\text{s}}(\text{COO})$], 1257(m), 1236(s), 1210(m) [$\delta(\text{OH})$], 1111(m) [$\nu(\text{C-O-C})$], 1034(s) [$\delta_{\text{ip}}(\text{C-H})$], 919(s), 801(m), 777(s) [$\delta_{\text{oop}}(\text{C-H})$], 752(s) [$\delta_{\text{oop}}(\text{C-H})$], 702(s), 686(m), 682(m), 583(m). UV-Vis (Methanol, $1.3 \cdot 10^{-3}$ M) λ_{max} (ϵ) = 727 (78) nm.

2.2.4. $[\text{Cu}(\text{Pip})_2(4\text{-Acpy})_2(\text{H}_2\text{O})] \cdot 3\text{MeOH} \cdot \text{H}_2\text{O}$ (**4a**)

To a solution containing 4-Acpy (37.9 mg, 0.313 mmol) in MeOH (10 mL), a green solution of **1** (100 mg, 0.156 mmol) in MeOH (30 mL) was added dropwise and stirred under reflux conditions for a day. The resulting dark green powder was filtered off, washed with 10 mL of cold methanol and dried under vacuum. Suitable blue crystals were obtained by slow evaporation of mother liquors on air for 14 days. The stoichiometry of this compound was definitely established after resolution of their X-ray crystal structure. However, the occluded solvent molecules are withdrawn from the structure after manipulation required for preparing the sample for EA yielding $[\text{Cu}(\text{Pip})_2(4\text{-Acpy})_2(\text{H}_2\text{O})]$ (**4b**).

4a. Yield: 98.2 mg (82%). $C_{33}H_{40}N_2O_{15}Cu$ (768.25 g/mol). ATR-FTIR (wavenumber, cm^{-1}): 3350(m) and 3265(m) [$\nu(O-H)$]_{MeOH} + [$\nu(O-H)$]_{water}, 3055(w) [$\nu_{ar}(C-H)$], 2917(m) [$\nu_{al}(C-H)$], 1696(s) [$\nu(C=O)$]_{4-AcPy}, 1660(w), 1568(s) [$\nu_{as}(COO)$], 1506(m), 1492(w), 1440(s), 1419(s) [$\nu_s(COO)$], 1357(s), 1258(s), 1242(s), 1227(s) [$\delta(OH)$], 1205(m), 1168(m), 1132(w), 1115(m) [$\nu(C-O-C)$], 1076(w), 1062(m), 1031(s) [$\delta_{ip}(C-H)$], 993(w), 962(w), 919(s), 891(m), 830(m), 819(s), 802(m), 777(s) [$\delta_{oop}(C-H)$], 721(m), 676(m), 592(s), 585(s). **4b.** Yield: 83.1 mg (82%). Elem. Anal. Calc. for $C_{30}H_{26}N_2O_{11}Cu$ (636.09 g/mol): C 55.09; H 4.01; N 4.28. Found: C 55.23; H 4.30; N 4.40%. ATR-FTIR (wavenumber, cm^{-1}): 3049(m) [$\nu_{ar}(C-H)$], 2919(w) [$\nu_{al}(C-H)$], 1699(s) [$\nu(C=O)$]_{4-AcPy}, 1622(s), 1558(s) [$\nu_{as}(COO)$], 1506(m), 1492(m), 1445(s), 1413(s), 1355(s), 1260(s), 1230(m), 1145(m), 1120(m) [$\nu(C-O-C)$], 1082(w), 1062(w), 1029(m) [$\delta_{ip}(C-H)$], 993(w), 961(w), 920(m), 870(m), 844(m), 821(m), 777(s) [$\delta_{oop}(C-H)$], 742(w), 696(m), 669(m). UV-Vis (Methanol, $9.9 \cdot 10^{-4}$ M) λ_{max} (ϵ) = 677 (68) nm.

2.2.5. $[Cu(Pip)_2(3,5-dmpz)_2]$ (**5**)

To a solution containing 3,5-dmpz (30.1 mg, 0.313 mmol) in MeOH (15 mL), a green solution of **1** (100 mg, 0.156 mmol) in MeOH (25 mL) was added dropwise and stirred under reflux conditions for 1 h. The solution was evaporated almost half of the volume and a violet powder was formed. The powder was filtered and washed with 10 mL of cold MeOH. Suitable violet crystals were obtained by slow evaporation of mother liquors on air for 5 days. Yield: 48.6 mg (53%). Elem. Anal. Calc. for $C_{38}H_{30}CuN_2O_9$ (586.05 g/mol): C 53.29; H 4.47; N 9.56. Found: C 53.17; H 4.35; N 9.45%. ATR-FTIR (wavenumber, cm^{-1}): 3186-3105(m) [$\nu(N-H)$], 3036(w) [$\nu_{ar}(C-H)$], 2929(w)-2879 [$\nu_{al}(C-H)$], 2783(w), 1631(w), 1604(w), 1557(s) [$\nu_{as}(COO)$], 1501(s), 1486(m), 1435(m) [$\nu_s(COO)$], 1381(s), 1341(s), 1300(m), 1257(m), 1240(s), 1189(m), 1166(w), 1143(w), 1113(m) [$\nu(C-O-C)$], 1075(w), 1059(m), 1034(s) [$\delta_{ip}(C-H)$], 989(w), 935(m), 921(s),

887(m), 825(m), 805(s), 775(s) [$\delta_{\text{oop}}(\text{C-H})$], 740(m), 721(m), 685(m), 665(w), 640(w), 593(m/s), 560(m). UV-Vis: (Methanol, $9.5 \cdot 10^{-4}$ M) $\lambda_{\text{max}} (\epsilon) = 714$ (13) nm.

2.2.6. $[\text{Cu}(\text{Pip})_2(\text{DMF})]_2 \cdot 2\text{DMF}$ (**6**)

Method A. To a colourless solution of HPip (51.9 mg, 0.313 mmol) in MeOH:DMF (2.5:1; 35 mL), the green powder of **1** (100 mg, 0.157 mmol) was added and stirred under reflux conditions at 120 °C for 48 h. The colour of the solution changed from green to dark blue. The resultant solution was treated with the sequential cooling-evaporation process under vacuum. The resulting green powder was filtered off, washed with 10 mL of cold methanol and dried on air. Suitable green crystals were obtained in two days by slow diffusion of hexane in a DMF solution of **6**. Yield: 112 mg (65%).

Method B. To a colourless solution of HPip (333 mg, 2.00 mmol) in MeOH:DMF (2.5:1, 50 mL), the green powder $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (200 mg, 1.00 mmol) was added portion wise and stirred under reflux conditions for 24 h. Colour change from green to dark blue. The resultant solution was treated as mentioned before. Yield: 40.5 mg (75%). Elem. Anal. Calc. for $\text{C}_{44}\text{H}_{48}\text{Cu}_2\text{N}_4\text{O}_{20}$ (1079.94 g/mol): C 48.93; H 4.48; N 14.01. Found: C 48.72; H 4.35; N 13.97%. ATR-FTIR (wavenumber, cm^{-1}): 2914(br) [$\nu_{\text{al}}(\text{C-H})$], 1678(m) [$\nu(\text{C=O})$]_{DMF}, 1661(m) [$\nu(\text{C=O})$]_{DMF}, 1630(m), 1589(m/s) [$\nu_{\text{as}}(\text{COO})$], 1497(m), 1487(m), 1437(s) [$\nu_{\text{s}}(\text{COO})$], 1381(s), 1259(s), 1242(s), 1112(m) [$\nu(\text{C-O-C})$], 1081(m), 1027(s) [$\delta_{\text{ip}}(\text{C-H})$], 917(s), 805(m), 773(s) and 679(s) [$\delta_{\text{oop}}(\text{C-H})$], 588(m). UV-Vis: (MeOH:DMF (2.5:1), $9.8 \cdot 10^{-4}$ M) $\lambda_{\text{max}} (\epsilon) = 717$ (76) nm.

2.2.7. $[\text{Cu}(\text{Pip})_2(2\text{-Bzpy})]_2$ (**7**)

Method A. To a green solution of **1** (100 mg, 0.156 mmol) and HPip (51.9 mg, 0.313 mmol) in MeOH (40 mL), a yellowish solution of 2-Bzpy (0.50 mL, 0.311 mmol) in MeOH

(10 mL) was added dropwise and stirred under reflux conditions for 73 h. The dark green solution was treated with sequential cooling-evaporating cycles and a green powder was formed. The powder was filtered. Suitable green crystals were obtained in five days by diffusion of the mother liquors in hexane. Yield: 50.5 mg (48%).

Method B. To a green solution of **6** (100 mg, 0.093 mmol) in MeOH (40 mL), a yellowish solution of 2-Bzpy (0.30 mL, 0.186 mmol) in MeOH (10 mL) was added dropwise and stirred under reflux conditions for 24 h. The resulting solution was evaporated under vacuum until dryness and oil was formed. Crude oil was washed several times with hexane and remains vacuumed until a dark green powder was obtained. Yield: 52.3 mg (50%). Elem. Anal. Calc. for $C_{56}H_{40}Cu_2N_2O_{16}$ (1125.99 g/mol): C 58.53; H 4.44; N 4.40. Found: C 58.39; H 4.33; N 4.31%. ATR-FTIR (wavenumber, cm^{-1}): 3082(w) [$\nu_{ar}(C-H)$], 2895(w) [$\nu_{al}(C-H)$], 1634(m), 1594(s) [$\nu_{as}(COO)$], 1569(m), 1501(m), 1486(m), 1437(s) [$\nu_s(COO)$], 1386(s), 1256(s), 1240(m), 1170(m), 1110(m) [$\nu(C-O-C)$], 1078(m), 1036(s) [$\delta_{ip}(C-H)$], 924(m), 877(w), 804(m), 770(s) [$\delta_{oop}(C-H)$], 743(m), 721(m), 700(m), 683(s) [$\delta_{oop}(C-H)$], 613(m), 584(m). UV-Vis: (MeOH, $1.1 \cdot 10^{-3}$ M) λ_{max} (ϵ) = 689 (86) nm.

2.3. X-ray single-crystal diffraction analysis

The crystallographic data of complexes **2-4a** and **5-7** are gathered in tables 1 and 2, respectively. Suitable crystals for X-ray diffraction were obtained by evaporation of mother liquors for **2-5**, by DMF:hexane diffusion for **6** and by MeOH:hexane diffusion for **7**. The X-ray intensity was measured on a D8 Venture system equipped with a multilayer mono-chromate and a Mo microfocus ($\lambda = 0.71073 \text{ \AA}$). A blue needle-like (**2-4a**), violet prism-like (**5**) and green prism-like (**6**, **7**) were used for the X-ray crystallographic analysis. Frames were integrated with the Bruker SAINT Software package using a narrow-frame algorithm. The structures were solved using the Bruker

SHELXTL Software, packaged and refined using SHELX (version-2018/3) [23]. Data were corrected for absorption effects using the multi-scan method (SADABS, version 2008/1). Crystal data and additional details of structure refinement for compounds **2-7** are included in the ESI (X-Ray crystal structures). Molecular graphics were generated using Mercury 3.9 software [24, 25]. Colour codes for all molecular graphics are: orange (Cu), blue (N), red (O), grey (C) and white (H). Crystal structure and molecular geometry is available in CIF format: CCDC 1851976-1851981 (**2-7**).

[Insert Table 1]

[Insert Table 2]

3. Results and discussion

3.1. General

The heteroleptic *core* compound $[\text{Cu}(\mu\text{-Pip})(\mu\text{-OAc})(\text{MeOH})]_2$ (**1**) was unexpectedly obtained in our group with 73% yield [18]. As a continuation of this study, in this paper the preparation and characterization of this compound with an 89% of yield is presented. The synthesis consists in the addition of solid $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ over the HPip in MeOH as solvent. Addition of acetic acid to the reaction media did not affect the reaction product (see experimental). As mentioned in the introduction section, there are few reported examples of Cu(II)-paddle-wheel complexes with heteroleptic *core* and their reactivity has not been described [8-11, 13, 14]. Herein, we present the reactivity study of a heteroleptic *core* compound with *N*-donor ligands.

Once **1** has been synthesised and full characterized, its reactivity against pyridine (py, **2**), 3-phenylpyridine (3-Phpy, **3**), 4-acetylpyridine (4-Acpy, **4a**) and 3,5-dimethylpyrazole (3,5-dmpz, **5**) in MeOH as solvent at r.t. (**2**, **3**) or reflux (**4a**, **5**) has been performed, resulting in four monomeric compounds: $[\text{Cu}((\text{Pip})_2(\text{dPy})_2(\text{H}_2\text{O}))]$ (dPy = py (**2**), 3-Phpy (**3**) and 4-Acpy (**4**)) and $[\text{Cu}(\text{Pip})_2(3,5\text{-dmpz})_2]$ (**5**) in moderate yields (48-82%). Compound **3** has been previously

reported by our research group [17] using a different synthetic approach and in a very low yield (12%). In opposite, here we synthesise it as powder with a 56% of yield. The reactivity of **1**, against *N*-donor ligands, shows that $[\text{Cu}(\mu\text{-Pip})(\mu\text{-OAc})]_2$ core is destroyed, resulting in monomeric compounds. The acetate ligands are displaced from **1**, regardless of the pyridine/pyrazole ligands used, and Pip ligands remain coordinated to the metal centre. In complexes **2-4a** the five-membered Cu(II) coordination sphere is completed by a water molecule and two pyridine derived ligands. In complex **5**, the six-membered coordination sphere is fulfilled by the pyrazole ligand and the bidentate chelate coordination mode of the two Pip ligands on its own (Scheme 1).

The reaction of **1** with HPip in MeOH:DMF (2.5:1) as solvent under reflux conditions yields $[\text{Cu}(\text{Pip})_2(\text{DMF})]_2 \cdot 2\text{DMF}$ (**6**). This compound displays a homoleptic core paddle-wheel structure with DMF molecules in the apical positions. Most interestingly, the reaction between **6** and 2-benzylpyridine (2-Bzpy) in MeOH as solvent under reflux conditions results in $[\text{Cu}(\text{Pip})_2(2\text{-Bzpy})]_2$ (**7**), which maintain its paddle-wheel structure (Scheme 1). Compound **7** is also obtained from **1** by its reaction with HPip in presence of 2-Bzpy.

All compounds were characterized by PXRD and analytical and spectroscopic techniques. Spectroscopic characterization details of all compounds are in the experimental section and in the S.I. For complexes **1-3**, **5-7**, phase purity of the bulk samples was confirmed by X-ray powder diffraction (S.I.: Fig. S1-S7). Elemental analyses for these compounds agree with the proposed formula. For compound **4**, X-ray powder diffraction and elemental analyses are in accordance with the formula $[\text{Cu}(\text{Pip})_2(4\text{-Acpy})_2(\text{H}_2\text{O})]$ (**4b**) due to the loss of solvent molecules (3 MeOH and H_2O).

The IR spectra of compounds **1-7** display the characteristic carboxylate bands in the range $1593\text{-}1550\text{ cm}^{-1}$ for $\nu_{\text{as}}(\text{COO})$ and $1442\text{-}1356\text{ cm}^{-1}$ for $\nu_{\text{s}}(\text{COO})$. The difference between these bands ($\Delta = \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$) [26, 27] for dimeric compounds **1**, **6** and **7** is 151 , 154 and 157 cm^{-1} , respectively, indicating a bridging coordination mode (S.I.: Fig.

S8, S13 and S14, respectively). For compounds **2–4** the values of Δ are 200, 207 and 212 cm^{-1} , respectively, corresponding to a monodentate coordination mode (S.I.: Fig. S9 – S11, respectively). Finally, for compound **5** this value is 122 cm^{-1} , which indicates a bidentate chelate coordination mode of the carboxylate moieties (S.I.: Fig. S12). The bands attributable to the aromatic groups, $\nu_{\text{as}}(\text{C}=\text{C})_{\text{ar}}$, $\nu_{\text{as}}(\text{C}=\text{N})_{\text{ar}}$, $\delta(\text{C}-\text{H})_{\text{ip}}$ and $\delta(\text{C}-\text{H})_{\text{oop}}$, are also present [28]. The presence of solvent molecules allows further identification of some specific bands. Compound **1** shows the $\nu(\text{O}-\text{H})_{\text{MeOH}}$ at 3301 cm^{-1} and **2–4** the $\nu(\text{O}-\text{H})_{\text{water}}$ bands appears in the range 3312–3241 cm^{-1} . Also the $\delta(\text{O}-\text{H})$ can be assigned in these four compounds. Moreover, for compounds **4** and **6**, bands attributable to $\nu(\text{C}=\text{O})$ from 4-Acpy (**4a**, **4b**) or DMF (**6**) units appear in the range 1696–1661 cm^{-1} . The IR spectral data, therefore, agree with the structures determined by the X-ray single-crystal diffraction method.

3.2. Structural studies

3.2.1. Crystal and extended structure of compounds **2–4a**

Compounds **2–4a** crystallize in the monoclinic $C2/c$ space group. They have a monomeric structure with a $[\text{CuO}_3\text{N}_2]$ core comprising a pair of each monodentate ligands, Pip and dpy (py (**2**) (Fig. 1a), 3-Phpy (**3**) (Fig. 1b) or 4-Acpy (**4a**) (Fig. 1c)) and a water molecule. There are more than 1,500 structures [29] with this core and only sixteen of these contain two oxygen atoms from a pair of carboxylates and one from a water molecule [5]. Five-coordinate compounds can adopt trigonal bipyramidal (D_{3h}), square-pyramidal (C_{4v}) or intermediate (C_{2v}) geometries. Several parameters are established to distinguish between them: the τ value which range from 1 (D_{3h}) to 0 (C_{4v}) [30], the $L_{\text{apical}}\text{-M-L}_{\text{basal}}$ angle (102° for C_{4v}) or the dihedral angles between the apical faces (53.1° for D_{3h} , 75.7° for C_{4v}) and the apical-basal faces (101.5° for D_{3h} , 119.8° for C_{4v}) [31]. All these compounds clearly exhibit a C_{4v} geometry, taking into account these

three factors: τ (0.205 (**2**), 0.053 (**3**), 0.282 (**4a**)), L-M-L angle (Cu-N1, 97.32° (**2**), Cu-N1, 93.58° (**3**), Cu-N1, 95.92° (**4a**)) and dihedral angles (apical faces: 60.22°-79.35° (**2**), 62.29°-76.24° (**3**), 61.16°-78.29° (**4a**); apical-basal: 120.11°-120.27° (**2**), 121.14°-121.02° (**3**), 120.58°-121.19° (**4a**)). The apical sites of the square-pyramidal geometries are occupied by water molecules (Cu-O5, 2.282(9) Å (**2**), 2.241(3) Å (**3**), 2.266(6) Å (**4a**)) while the basal plane contains the supplementary ligands in *trans* disposition.

[Insert Figure 1]

[Insert Table 3]

All the Cu-O and Cu-N distances for the three compounds are in the same order as described in the literature [17, 32-36] (Table 3). For **2**, Cu(II) ion is 0.109 Å displaced out of the basal plane towards the axial site while in **3** and **4a**, Cu(II) ion is displaced 0.029 Å and 0.062 Å, respectively. The twisting of the *N*-donor ligands produces these displacements and deviation increases **2** > **4a** > **3**.

Compounds **2-4a**, present supramolecular 1D-chains (**2**, **3**) along the *b* axis (Fig. 2a and 3a, respectively) or 2D-layers (**4a**) along the *bc* plane (Fig. 4a).

[Insert Figure 2]

[Insert Figure 3]

[Insert Figure 4]

The 1D linear chain formation is supported by two bridging symmetrically interactions in which apical water molecule acts as a heteromeric intermolecular synthon through hydrogen bond interaction with the non-coordinated carboxylate oxygen atoms. These hydrogen bond interactions are moderately strong with D-H...A distances (O5-H5...O2, 1.90(15) Å (**2**); 1.87(2) Å (**3**); 1.97(8) Å (**4a**)) and bond angles (167(18)° (**2**), 170(3)° (**3**), 172(14)° (**4a**)), which are characteristic of strong interactions [37]. Moreover, compound **2** presents a hydrogen bond interaction between one dioxole oxygen atom of a piperonylate moiety and the hydrogen of a neighboring

stacked in a row piperonylate aromatic ring (C9-H9...O4, 2.325(8) Å, 166(18)°). This interaction is driven by the carboxylates spatial disposition that supports the supramolecular expansion (Fig. 2b). In contrast, the twisting of the Pip units in **3** and **4a** confers a too forced angle (C18-H18...O3, 2.655 Å, 127.58°(3) and C7-H7...O3, 2.646 Å, 133.95°(4a)) and avoids the H-bond interaction formation (Fig. 3b). Furthermore, the addition of the acetyl group in **4a** allows the formation of supplementary interactions: one aliphatic hydrogen of the acetyl group interacts with the oxygen atom of the dioxole ring propagating the 1D chain along the c axis and forming 2D layers along the bc plane. Interestingly, there are few structures with similar 1D chain with a double H-bond interaction belonging from water – carboxylate [17, 32-36], which distinguishes compound **4a** from the rest is the presence of three methanol and one occluded water molecules. Its supramolecular 2D square-grid extended structure (Fig. 4b) generates channels that are filled by guest methanol and water solvent molecules. The solvent accessible volume of these channels is a 6.2% of the cell volume. On standing in air, the guest solvent is lost, as indicated by elemental analysis results, although aqua ligand is not. PXRD of the aerated sample denotes that the initial crystal structure has been modified (S.I.: Fig. S4). Unfortunately, these changes seem to provoke the collapse of the pores, and the materials does not adsorb any significant amount of nitrogen.

3.2.2. Crystal and extended structure of compound **5**

Compound **5** crystallizes in the triclinic *P*-1 space group with two crystallographically independent units enclosed in the unit cell (molecules **A** and **B**). Each unit has a monomeric structure with a [CuO₄N₂] core (Figure 5a) comprising a pair of carboxylate units with a *syn-syn* chelate array (Cu-O 1.965 Å - 2.653 Å) and a pair of monodentate 3,5-dmpz moieties (Cu-N 1.975 Å - 1.977 Å). It has an inversion center at the metal node, which relates the two carboxylates and the two 3,5-dmpz ligands. This compound

presents a distorted octahedral molecular geometry with a significant $O_{ax}-Cu-O_{eq}$ angle deviation (**A**, 55.02° and 124.98°; **B**, 55.90° and 124.10°). The equatorial plane is comprised by two shorter distance carboxylate oxygen atoms (O1A and O1B) and two pyrazolic nitrogen atoms (N1A and N1B), which are in range of other reported compounds described in the literature $[Cu(Hdmpz)_2(L)_2]$ ($L = 4\text{-methylbenzoate}$, 3-methylbenzoate , 2-chlorobenzoate , 4-methoxybenzoate [3]; $[Cu(C_4H_4O_5)(C_5H_8N_2)_2(H_2O)] \cdot 2H_2O$ [38], $[Cu_4Cl_2(oxalate)(pz)_2((1\text{-hydroxymethyl)pyrazole})_2]_n$ [39] (Table 4). The asymmetric furthest oxygen atoms [40–44], which are typically generated in chelate carboxylates due to the Jahn-Teller effect [45] occupy the axial sites. In addition, this six coordinate array is underpinned by the elongation of the C-O carboxylic bond length (C1A-O2A 1.247 Å, C1B-O2B 1.248 Å) respect to the C-O bond of the uncoordinated piperonylic acid (1.214 - 1.223 Å), clearly suggesting that this oxygen is coordinated [44].

The propagation of intermolecular interactions defines 1D chains along the a axis with all the ligands stacked in a row (Figure 5b). The main association in this system is the N -pyrazolic donor-carboxylate, which generates a double H-bond interaction. The protonated nitrogen of the pyrazole ring interacts with the coordinated carboxylic oxygen of the asymmetric chelate with the largest Cu-O distance (N2A-H2A...O2A, 1.940(14) Å, 154.10° (15)) forming this kind of supramolecular chains (Table 5).

[Insert Figure 5]

[Insert Table 4]

[Insert Table 5]

3.2.3. Crystal structures of compounds **6** and **7**

Compounds **6** (Fig. 6a) and **7** (Fig. 6b) crystallize in the triclinic $P\bar{1}$ space group. These compounds are dimers with four symmetrically located ligand moieties orientated in a *syn-syn* bidentate bridging mode with the carboxylic oxygen atoms coordinating two Cu(II) nodes and

anchoring the paddle-wheel-like structure. In both compounds, each Cu(II) node has a square-pyramidal geometry consisting an one apical DMF (**6**) or 2-Bzpy (**7**) moiety and four oxygen atoms from the bridging carboxylate groups at the basal plane.

[Insert Figure 6]

Selected distances and angles are provided in Table 6. Compound **6** has the apical units (Cu1-O9) at 2.1540(15) Å while compound **7** (Cu1B-N1B) at 2.243(8) Å. The remaining Cu-O distances of the basal plane are in the range 1.959(6) Å and 1.982(7) Å, which are shorter than apical N atoms due to the Jahn-Teller effect [45] but comparable to similar paddle-wheel structures described in the literature (1.945 Å to 2.008 Å) [17, 22, 46-51].

[Insert Table 6]

For compound **7**, two crystallographically independent dimeric molecules (**A** and **B**) are present in the unit cell.

In both structures, Cu(II) ions are displaced from the oxygen atoms plane (0.182 Å (**6**); 0.212 Å (**7**)) towards the apical position. In addition, the square base angles range from 87.45° to 169.37° with a slight deviation of the square-planar geometry ($\tau = 0.0035$ (**6**) and $\tau = 0.0072$ (**7**)) [33]. The Cu...Cu intermolecular distances are 2.6057(5) Å and 2.656(1) Å, (**6** and **7**, respectively). In **6**, this Cu...Cu distance is a little bit shorter than other similar structures (2.610 Å-2.713 Å) [17, 22, 45-50]. It is worthwhile to mention that compound **7** presents the largest angle (O2A-Cu1A-N1A, 99.40°) which corresponds to the carboxylate oxygen closest to the 2-Bzpy ligand. The steric hindrance of the benzyl rings could promote its orientation and the angle opening of the nearest carboxylate ligand (Fig. 6b).

3.2.4. Extended structures of compounds **6** and **7**

For compound **6**, all the intermolecular interactions are based on coordinated and the uncoordinated DMF molecules. The first intermolecular interaction is the homomeric asymmetric amide–amide interaction between them (C5–H5B...O9, 2.407(3) Å; C5–H5B, 0.9900(14) Å; H5B–C5...O9, 3.314(4) Å, 152.11°(6)). The following interactions are between aliphatic proton from each of two Pip units and an uncoordinated DMF molecule through its carboxylic oxygen atom, which also interacts with a coordinated DMF of a neighbouring paddle-wheel forming 1D chains along the *a* axis (C19–H19B...O10, 2.102(4) Å; C19–H19, 0.9800(14) Å; H19B–C19...O19, 3.036(4) Å, 158.54°(6)) (Fig. 7a). The remaining pair of Pip units interacts directly with a coordinated DMF molecule of other neighbouring paddle-wheel (Fig. 7b) generating 2D layers along the (00½) plane (C13–H13A...O10, 2.163(4) Å; C13–H13A, 0.9900(16) Å; H13A–C13...O10, 3.096(3) Å, 156.57°(7)). For compound **7**, the 2D supramolecular structure is generated by the propagation in the *bc* plane through two alternated simultaneous hydrogen bond interactions. Each dimeric unit possesses four propagation centres, two from the 2-Bzpy units (Fig. 8a) and two from the piperonylate units (Fig. 8b). These two crystallographically different 2-Bzpy rings interacts with the oxygen atoms of the neighbouring dioxole Pip rings (C16–H16...O8, 2.511(3) Å; C16–H16 0.9500(14) Å; H16–C16...O8, 3.213(3) Å and C4–H4...O15, 2.513(3) Å; C4–H4 0.9500(14) Å; H4–C4...O15, 3.165(3) Å) and constructing 2D layer.

[Insert Figure 7]

[Insert Figure 8]

3.3. UV-Vis spectroscopy

UV-Vis electronic spectra for all the compounds have been recorded in methanol (**1**–**5**, **7**) or MeOH:DMF (2.5:1) (**6**) as solvent. All spectra show one band in the visible region, between 727 and 677 nm with $\epsilon = 13$ –124 M⁻¹ cm⁻¹ (S.I.: Fig. S15). For a d⁹ ion,

with a 2D term, there is only one transition between the two levels 2E_g and $^2T_{2g}$. In the octahedral crystalline field, the spin-orbital coupling unfolds the $^2T_{2g}$ level in two sublevels due to its tetragonal distortion (Jahn-Teller effect). For these reason, an octahedral d^9 ion has two possible transitions, both from the 2E_g level to each of the unfolded $^2T_{2g}$ sublevels giving two absorption bands. However, in the case of Cu(II) these sublevels are energetically close and the difference in energy is too small to discriminate between them resulting in a broad band [52, 53]. The energy of these electronic transitions depends on the fulfilment of the two selection rules (Laporte and spin). Electronic transitions in d^9 Cu(II) complexes only accomplish the spin rule, for this reason the energy of this transitions is lower than other transition metal complexes and its ϵ values range from 10 to 200 mol⁻¹ cm⁻¹. The obtained values for compound **1-7** are in accordance with the values reported in the literature for similar Cu(II) complexes (Table 7) [18, 54-57].

[Insert Table 7]

4. Conclusions

The reactivity of the heteroleptic *core* compound **1** with selected supplementary ligands (py, 3-Phpy, 4-Acpy and 3,5-dmpz) results in the rupture of the dimeric array and yields four monomeric species (**2-5**). In opposite, the reaction between the homoleptic *core* compound **6** with the 2-Bzpy ligand yield the dimeric compound **7**, keeping the paddle-wheel building unit. It is worthwhile to mention that even there are similar heteroleptic *core* previously described in the literature [6-16]; there are few studies about their reactivity. In this juncture, besides presenting the first trial in this sense, it is also remarkable the different behaviour exhibited by the two paddle-wheel compounds (**1**, **6**). This difference can only be promoted by the fact of having mixed bridges.

Conflicts of interest

There are no conflicts to declare.

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Appendix A. Supplementary material

CCDC: 1851976-1851981 contain the supplementary crystallographic data for compounds **2-7**. The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax:(+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

PXRD patterns and additional ATR-FTIR spectra figures are available as electronic supplementary information in the online version.

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Scheme 1. Schematic synthesis of the compounds **1-7**.

Table 1. Crystallographic data for compounds **2-4**.

	2	3	4
Empirical formula	C ₂₆ H ₂₂ CuN ₂ O ₉	C ₃₈ H ₃₀ CuN ₂ O ₉	C ₃₃ H ₄₀ CuN ₂ O ₁₅
Formula weigh	569.99	722.20	768.21
T (K)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
System, space group	Monoclinic, C 2/c	Monoclinic, C 2/c	Monoclinic, C 2/c
Unit cell dimensions			
a (Å)	15.530(3)	22.6648(13)	23.1610(17)
b (Å)	6.1225(12)	5.7527(3)	5.8928(4)
c (Å)	25.132(5)	23.9870(16)	26.0634(19)
α (°)	90	90	90
β (°)	91.533(6)	95.958(4)	110.439(2)
γ (°)	90	90	90
V (Å ³)	2388.7(8)	3110.6(3)	3333.3(4)
Z	4	4	4
D _{calc} (g cm ³)	1.585	1.542	1.531
μ (mm ⁻¹)	0.975	0.767	0.733
F(000)	1172	1492	1604
Crystal size (mm ³)	0.297x0.063x0.062	0.707x0.101x0.038	0.179x0.068x0.032
hkl ranges	-17≤h≤18 -7≤k≤7 -29≤l≤29	-29≤h≤29 -7≤k≤7 -31≤l≤31	-23≤h≤23 -6≤k≤6 -26≤l≤26
2θ range (°)	3.048 to 24.446		
Reflections collected/ unique/[R _{int}]	8490/1953 [R _{int} = 0.0449]	32090/3576 [R _{int} =0.1365]	51462/1898 [R _{int} = 0.0691]
Completeness to θ = 25.242°	99.1 %	99.9 %	63.0 %
Absorption Correction	Semi-empirical	Semi-empirical	Semi-empirical
Max. and min. transmis.	0.7451 and 0.6333	0.7456 and 0.6731	0.7446 and 0.6930
Refinement method	Full matrix least- squares on F ²	Full matrix least- squares on F ²	Full matrix least- squares on F ²
Data/restraints/parameters	1953/1/159	3576/0/230	1898/5/222
Goodness of fit (GOF) on F ²	1.134	1.056	1.084
Final R indices [I>2σ(I)]	R1 =0.0853, wR2 = 0.2283	R1 =0.0518, wR2 = 0.0960	R1 =0.0675, wR2 = 0.1757
R indices (all data)	R1 = 0.0916, wR2 = 0.2320	R1 = 0.0849 wR2 = 0.1073	R1 = 0.0735 wR2 = 0.1813
Extinction coefficient	n/a	n/a	n/a
Largest. Diff. peak and hole (e Å ⁻³)	2.324 and -1.830	0.423 and -0.661	1.623 and -0.761

Table 2. Crystallographic data for compounds 5-7.

	5	6	7
Empirical formula	C ₂₆ H ₂₆ CuN ₄ O ₈	C ₄₄ H ₄₈ Cu ₂ N ₄ O ₂₀	C ₅₆ H ₄₂ Cu ₂ N ₂ O ₁₆
Formula weigh	586.05	1079.94	1125.99
T (K)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
System, space group	Triclinic, P -1	Triclinic, P-1	Monoclinic, P21/c
Unit cell dimensions			
a (Å)	6.0789(2)	10.4359(5)	17.0709(6)
b (Å)	12.4827(4)	11.1697(5)	18.5452(7)
c (Å)	17.7198(6)	12.1119(6)	15.3980(5)
α (°)	73.0490(10)	87.276(2)	90
β (°)	83.9550(10)	65.220(2)	99.8320(10)
γ (°)	86.468(2)	64.078(2)	90
V (Å ³)	1278.35(7)	1136.84(10)	4803.2(3)
Z	2	1	4
Dcalc (g cm ³)	1.523	1.577	1.557
μ (mm ⁻¹)	0.913	1.023	0.965
F(000)	606	558	2312
Crystal size (mm ³)	0.236x0.138x0.081	0.233x0.158x0.155	0.278x0.082x0.045
hkl ranges	-7≤h≤7 -15≤k≤15 -22≤l≤22	-14≤h≤13 -15≤k≤15 -17≤l≤17	-22≤h≤22 -24≤k≤24 -20≤l≤20
2θ range (°)	2.413 to 26.728	2.421 to 30.557	2.422 to 28.332
Reflections collected/ unique/[Rint]	29716/5397 [R(int) = 0.0345]	46461/6939 [R(int) = 0.0305]	122091/11916 [R(int) = 0.0495]
Completeness to θ = 25.242°	99.6 %	99.7 %	99.4 %
Absorption Correction	Semi-empirical	Semi-empirical	Semi-empirical
0.7454 and 0.6940	0.7454 and 0.6940	0.7461 and 0.6897	0.7457 and 0.06985
Refinement method	Full matrix least- squares on F ²	Full matrix least- squares on F ²	Full matrix least- squares on F ²
Data/restraints/parameters	5397/0/359	6939/0/317	11916/1/685
Goodness of fit (GOF) on F ²	1.020	1.036	1.048
Final R indices [I>2σ(I)]	R1 = 0.0293, wR2 = 0.0714	R1 = 0.0427, wR2 = 0.1060	R1 = 0.0359 wR2 = 0.0893
R indices (all data)	R1 = 0.0384, wR2 = 0.0761	R1 = 0.0516, wR2 = 0.1119	R1 = 0.0488 wR2 = 0.0976
Extinction coefficient	n/a	n/a	n/a
Largest. Diff. peak and hole (e Å ⁻³)	0.464 and -0.419	1.480 and -1.465	0.623 and -0.567

Table 3. Selected bond lengths (Å) and bond angles (°) for compounds **2** – **4a**.

2			
Bond length (Å)			
Cu(1)-O(1)	1.937(5)	Cu(1)-N(1)	2.018(6)
Cu(1)-O(1)#1	1.937(5)	Cu(1)-N(1)#1	2.017(6)
Cu(1)-O(5)	2.282(9)		
Bond angles (°)			
O(1)#1-Cu(1)-O(1)	177.7(3)	O(1)#1-Cu(1)-N(1)#1	90.5(2)
O(1)#1-Cu(1)-O(5)	88.86(16)	N(1)#1-Cu(1)-O(5)	97.3(2)
O(1)#1-Cu(1)-N(1)	89.8(2)	N(1)-Cu(1)-N(1)#1	165.5(4)
O(1)#1-Cu(1)-O(5)	88.86(16)		
3			
Bond length (Å)			
Cu(1)-O(1)	1.9379(19)	Cu(1)-N(1)	2.020(2)
Cu(1)-O(1)#1	1.9380(19)	Cu(1)-N(1)#1	2.020(2)
Cu(1)-O(5)	2.241(3)		
Bond angles (°)			
O(1)-Cu(1)-O(1)#1	176.06(14)	O(1)-Cu(1)-O(5)	88.03(7)
O(1)-Cu(1)-N(1)	91.72(9)	N(1)-Cu(1)-O(5)	93.62(8)
O(1)#1-Cu(1)-N(1)	88.53(9)	N(1)#1-Cu(1)-O(5)	93.62(8)
N(1)-Cu(1)-N(1)#1	172.77(15)		
4a			
Bond length (Å)			
Cu(1)-O(1)	1.928(4)	Cu(1)-N(1)	2.023(5)
Cu(1)-O(1)#1	1.928(4)	Cu(1)-N(1)#1	2.023(5)
Cu(1)-O(5W)	2.266(6)		
Bond angles (°)			
O(1)-Cu(1)-O(1)#1	174.9(3)	O(1)-Cu(1)-O(5W)	87.47(13)
O(1)#1-Cu(1)-N(1)#1	91.64(18)	N(1)#1-Cu(1)-O(5W)	95.92(15)
O(1)#1-Cu(1)-N(1)	88.88(18)	N(1)-Cu(1)-N(1)#1	168.2(3)

2: #1 -x+1,y,-z+3/2; **3:** #1 -x+1,y,-z+1/2; **4:** #1 -x+1,y,-z+1/2;

Table 4. Selected bond lengths (Å) and bond angles (°) for compound 5.

5			
Bond length (Å)			
Cu(1A)-O(1A)#1	1.9654(12)	Cu(1B)-O(1B)#2	1.9672(12)
Cu(1A)-O(2A)	2.6536(14)	Cu(1B)-O(2B)	2.6138(14)
Cu(1A)-N(1A)#1	1.9749(15)	Cu(1B)-N(1B)#2	1.9769(15)
Bond angles (°)			
O(1A)#1-Cu(1A)-O(1A)	180	O(1B)#2-Cu(1B)-O(1B)	180
O(1A)#1-Cu(1A)-N(1A)	89.78(6)	O(1B)#2-Cu(1B)-N(1B)	89.74(6)
O(1A)#1-Cu(1A)-N(1A)#1	90.22(6)	O(1B)#2-Cu(1B)-N(1B)#2	90.26(6)
N(1A)-Cu(1A)-N(1A)#1	180	N(1B)-Cu(1B)-N(1B)#2	180

5: #1 -x,-y,-z+1 #2 -x+2,-y+1,-z+2

Table 5. Selected intermolecular interactions for compounds 2-5.

2	H...A (Å)	D...A (Å)	D-H (Å)	>D-H...A (°)
O5-H5O...O2	1.90(15)	2.802(8)	0.92(12)	167(18)
C9-H9...O4	2.325(8)	3.253(15)	0.9500	166(18)
3				
O5-H5O...O2	1.87(2)	2.711(3)	0.85(3)	170(3)
4a				
O5W-H5W...O2	1.967(8)	2.765(13)	0.804(10)	171.62(14)
C15-H15B...O3	2.470(12)	3.433(14)	0.9800(12)	167.74(14)
5				
N2A-H2A...O2A	1.940(14)	2.7588(12)	0.8800(14)	154.10(15)
N2B-H2B...O2B	1.977(14)	2.7615(12)	0.8800(14)	147.76(15)

Table 6. Selected bond lengths (Å) and bond angles (°) for compounds **6** and **7**.

6			
Bond length (Å)			
Cu(1)-O(5)#1	1.9633(14)	Cu(1)-O(2)#1	1.9727(13)
Cu(1)-O(1)	1.9669(13)	Cu(1)-O(9)	2.1540(15)
Cu(1)-O(6)	1.9695(14)	Cu...Cu	2.6057(5)
Bond angles (°)			
O(5)#1-Cu(1)-O(1)	88.98(6)	O(6)-Cu(1)-O(9)	92.64(6)
O(5)#1-Cu(1)-O(6)	169.37(6)	O(2)#1-Cu(1)-O(9)	95.08(6)
O(1)-Cu(1)-O(6)	91.69(6)	O(5)#1-Cu(1)-Cu(1)#1	89.85(5)
O(5)#1-Cu(1)-O(2)#1	88.44(6)	O(1)-Cu(1)-Cu(1)#1	83.70(4)
O(1)-Cu(1)-O(2)#1	169.17(6)	O(6)-Cu(1)-Cu(1)#1	79.68(4)
O(6)-Cu(1)-O(2)#1	88.94(6)	O(2)#1-Cu(1)-Cu(1)#1	85.78(4)
O(5)#1-Cu(1)-O(9)	97.86(6)	O(9)-Cu(1)-Cu(1)#1	172.26(5)
O(1)-Cu(1)-O(9)	95.69(6)		
7			
Bond length (Å)			
Cu(1)-O(6)	1.9516(14)	Cu(2)-O(13)	1.9598(14)
Cu(1)-O(14)	1.9588(14)	Cu(2)-O(5)	1.9722(14)
Cu(1)-O(2)	1.9731(14)	Cu(2)-O(9)	1.9773(14)
Cu(1)-O(10)	1.9785(14)	Cu(2)-O(1)	1.9835(14)
Cu(1)-N(1)	2.1999(16)	Cu(2)-N(2)	2.2484(16)
		Cu(1)...Cu(2)	2.6910(3)
Bond angle (°)			
O(6)-Cu(1)-O(14)	166.18(6)	O(13)-Cu(2)-O(5)	167.61(6)
O(6)-Cu(1)-O(2)	89.11(7)	O(13)-Cu(2)-O(9)	87.99(6)
O(14)-Cu(1)-O(2)	88.84(7)	O(5)-Cu(2)-O(9)	91.71(6)
O(6)-Cu(1)-O(10)	90.28(6)	O(13)-Cu(2)-O(1)	88.68(7)
O(14)-Cu(1)-O(10)	88.87(7)	O(5)-Cu(2)-O(1)	88.51(6)
O(2)-Cu(1)-O(10)	167.89(6)	O(9)-Cu(2)-O(1)	165.36(6)
O(6)-Cu(1)-N(1)	95.73(6)	O(13)-Cu(2)-N(2)	99.01(6)
O(14)-Cu(1)-N(1)	98.08(6)	O(5)-Cu(2)-N(2)	93.11(6)
O(2)-Cu(1)-N(1)	101.49(6)	O(9)-Cu(2)-N(2)	103.37(6)
O(10)-Cu(1)-N(1)	90.60(6)	O(1)-Cu(2)-N(2)	91.23(6)

6: #1-x+2,-y,-z+1

Table 7. UV-Vis spectroscopy data of compounds **1-7** and similar examples of the literature.

Compound	Geometry	$\lambda_{\max}$ (nm)	ϵ (M ⁻¹ cm ⁻¹)	Ref.
[Cu(dien)(pnb) ₂] $\cdot$ H ₂ O	sqp	615	194	[54]
[Cu(dien) ₂](pnb) ₂	Oh	618	120	[54]
[Cu(dien)(pnb)(H ₂ O)] $\cdot$ (pnb) $\cdot$ (Hpnb)	sqp	608	140	[54]
[Cu(en) ₂ (H ₂ O) ₂] $\cdot$ (2-PBA) ₂ $\cdot$ 2H ₂ O	Oh	546	-	[55]
[Cu(en) ₂ (H ₂ O)] $\cdot$ (DPA) ₂ $\cdot$ 3H ₂ O	sqp	535	-	[55]
[TMpA)CuCl] ⁺	bpt	725	90	[56]
[(BPQA)CuCl] ⁺	sqp	700	106	[56]
[(BQPA)CuCl] ⁺	sqp	737	137	[56]
[(TMQA)CuCl] ⁺	sqp	691	185	[56]
[Cu(μ -Pip)(μ -Ac)(MeOH)] ₂ (1)	sqp	716	124	[18]
[Cu(Pip) ₂ (py) ₂ (H ₂ O)] (2)	sqp	710	33	work
[Cu(Pip) ₂ (3-Phpy) ₂ (H ₂ O)] (3)	sqp	727	78	work
[Cu(Pip) ₂ (4-Acpy) ₂ (H ₂ O)] (4)	sqp	677	68	work
[Cu(Pip) ₂ (3,5-dmpz) ₂] (5)	Oh	714	13	work
[Cu(μ -Pip) ₂ (DMF)] $\cdot$ 2DMF (6)	sqp	717	76	work
[Cu(μ -Pip) ₂ (2-Bzpy)] (7)	sqp	689	86	work

dien= diethylenetriamine; Hpnb= p-nitrobenzoic acid; en= ethylenediamine; PBA= phenoxybenzoate; DPA= diphenylacetate; TMpA= =tris[(((2-pyridyl)methyl))- methylamine; BPQA= 1-(pyridin-2-yl)-N-(pyridin-2-ylmethyl)-N-(quinolin-2-ylmethyl)methanamine; BQPA= 1-(pyridin-2-yl)-N,N-bis(quinolin-2-ylmethyl)methanamine; TMQA= 1-(isoquinolin-3-yl)-N,N-bis(quinolin-2-ylmethyl)methanamine. bpt = trigonal-bipyramidal; sqp = square-pyramidal; Oh = octahedral

Figure 1. Molecular structure of $[\text{Cu}(\text{Pip})_2(\text{dPy})_2(\text{H}_2\text{O})]$ (**a** $\text{dPy}=\text{py}$ (**2**); **b** 3-Phpy (**3**); **c** 4-Acpy (**4a**)) complexes showing an atom labelling scheme. The hydrogen atoms are omitted for clarity.

Figure 2. **a.** *a* axis view of the one-dimensional ordering of the [Cu(Pip)₂(py)₂(H₂O)] (2) complex by water-carboxylate hydrogen bonding through the *b* axis. **b.** Piperonylate ligands stacked in a row disposition allows its intermolecular C-H...O hydrogen bonding interactions.

Figure 3. **a.** *a* axis view of the one-dimensional ordering of the $[\text{Cu}(\text{Pip})_2(3\text{-Phpy})_2(\text{H}_2\text{O})]$ (3) complex by water-carboxylate hydrogen bonding through the *b* axis. **b.** Piperonylates planarity drifting disposition prevent its intermolecular C-H $\cdots$ O hydrogen bonding. Only hydrogens involved in the intermolecular interaction are shown.

Figure 4. **a.** a axis view of the one-dimensional ordering of the $[\text{Cu}(\text{Pip})_2(4\text{-AcPy})_2(\text{H}_2\text{O})] \cdot 3\text{MeOH} \cdot \text{H}_2\text{O}$ (**4a**) complex by water-carboxylate hydrogen bonding through the b axis. **b.** b axis view of the propagation through the bc plane by hydrogen bonding between the oxygen of the piperonylate units and the protons of the acetyl groups. Solvent molecules are omitted for clarity.

Figure 5. **a.** Molecular structure of [Cu(Pip)₂(3,5-dmpz)₂] (5) complex showing an atom labelling scheme. The hydrogen atoms are omitted for clarity. **b.** *b* axis view of the one-dimensional ordering of the [Cu(Pip)₂(3,5-dmpz)₂] (5) complex by a double pirazole-carboxylate hydrogen bonding forming 1D chains. Only hydrogen atoms involved in the intermolecular interactions are shown.

Figure 6. **a.** Molecular structure of $[\text{Cu}(\text{Pip})_2(\text{DMF})_2]$ (**6**). **b.** Molecular structure of $[\text{Cu}(\text{Pip})_2(2\text{-Bzpy})]_2$ (**7**) complexes showing an atom labelling scheme. The hydrogen atoms are omitted for clarity.

Figure 7. **a.** b axis view of the one-dimensional ordering through the coordinated DMF molecules and the Pip rings of the $[\text{Cu}(\text{Pip})_2(\text{DMF})]_2$ (**6**). **b.** ab view of the one-dimensional ordering through the uncoordinated DMF molecules joining two dimeric units of $[\text{Cu}(\text{Pip})_2(\text{DMF})]_2 \cdot 2\text{DMF}$. Only hydrogen atoms from DMF molecules and those involved in the intermolecular interaction are shown.

Figure 8. **a** and **b** shows the C-H...O hydrogen bonding formation of compound **7** between the Pip rings and the pyridil ring of the 2-Bzpy units forming the 2D layers. **a.** (1/3 1/2 1) view and **b.** (1/3 1 1/2) view of these weak interactions.

Captions of Figures

Figure 1. Molecular structure of $[\text{Cu}(\text{Pip})_2(\text{dPy})_2(\text{H}_2\text{O})]$ (**a** $\text{dPy}=\text{py}$ (**2**); **b** 3-Phpy (**3**); **c** 4-Acpy (**4**)) complexes showing an atom labelling scheme. The hydrogen atoms are omitted for clarity.

Figure 2. a. *a* axis view of the one-dimensional ordering of the $[\text{Cu}(\text{Pip})_2(\text{py})_2(\text{H}_2\text{O})]$ (**2**) complex by water-carboxylate hydrogen bonding through the *b* axis. **b.** Piperonylate ligands stacked in a row disposition allows its intermolecular $\text{C-H}\cdots\text{O}$ hydrogen bonding interactions.

Figure 3. a. *a* axis view of the one-dimensional ordering of the $[\text{Cu}(\text{Pip})_2(3\text{-Phpy})_2(\text{H}_2\text{O})]$ (**3**) complex by water-carboxylate hydrogen bonding through the *b* axis. **b.** Piperonylates planarity drifting disposition prevent its intermolecular $\text{C-H}\cdots\text{O}$ hydrogen bonding. Only hydrogens involved in the intermolecular interaction are shown.

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Supporting Information

Reactivity of homoleptic and heteroleptic core paddle wheel Cu(II) compounds

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Powder X-Ray Diffraction Patterns

Figure S1. PXRD of $[\text{Cu}(\mu\text{-Pip})(\mu\text{-Ac})(\text{MeOH})]_2$ (1). Simulated (top) and experimental (bottom).

Figure S2. PXRD of $[\text{Cu}(\text{Pip})_2(\text{py})_2(\text{H}_2\text{O})]$ (2). Simulated (top) and experimental (bottom).

Figure S3. PXRD of $[\text{Cu}(\text{Pip})_2(3\text{-Phpy})_2(\text{H}_2\text{O})]$ (**3**). Simulated (top) and experimental (bottom).

Figure S4. PXRD of $[\text{Cu}(\text{Pip})_2(4\text{-Acpy})_2(\text{H}_2\text{O})] \cdot 3\text{MeOH} \cdot \text{H}_2\text{O}$ (**4a**), simulated (top). PXRD of $[\text{Cu}(\text{Pip})_2(4\text{-Acpy})_2(\text{H}_2\text{O})]$ (**4b**), experimental (bottom).

Figure S5. PXRD of $[\text{Cu}(\text{Pip})_2(3,5\text{-dmpz})_2]$ (5). Simulated (top) and experimental (bottom).

Figure S6. PXRD of $[\text{Cu}(\text{Pip})_2(\text{DMF})_2]_2 \cdot 2\text{DMF}$ (**6**). Simulated (top) and experimental starting from copper acetate (method B, middle) or from **1** (method A, bottom).

Figure S7. PXRD of $[\text{Cu}(\text{Pip})_2(2\text{-Bzpy})]_2$ (7). Simulated (top) and experimental (bottom).

Infrared spectroscopy

Figure S8. ATR-FTIR spectrum of $[\text{Cu}(\mu\text{-Pip})(\mu\text{-OAc})(\text{MeOH})]_2$ (**1**).

Figure S9. ATR-FTIR spectrum of $[\text{Cu}(\text{Pip})_2(\text{py})_2(\text{H}_2\text{O})]$ (2).

Figure S10. ATR-FTIR spectrum of [Cu(Pip)₂(3-Phpy)₂(H₂O)] (3).

Figure S11. **a.** ATR-FTIR spectrum of $[\text{Cu}(\text{Pip})_2(4\text{-Acpy})_2(\text{H}_2\text{O})]\cdot 3\text{MeOH}\cdot \text{H}_2\text{O}$ (**4a**). **b.** ATR-FTIR spectrum of $[\text{Cu}(\text{Pip})_2(4\text{-Acpy})_2(\text{H}_2\text{O})]$ (**4b**), corresponding to the powder after vacuum conditions. It can be appreciated the disappearance of the $[\nu(\text{O-H})]$ bands at 3350 and 3265 cm^{-1} .

Figure S12. ATR-FTIR spectrum of [Cu(Pip)₂(3,5-dmpz)₂] (5).

Figure S13. ATR-FTIR spectrum of $[\text{Cu}(\text{Pip})_2(\text{DMF})_2]_2 \cdot 2\text{DMF}$ (**6**).

Figure S14. ATR-FTIR spectrum of $[\text{Cu}(\text{Pip})_2(2\text{-Bzpy})]_2$ (7).

UV-Vis spectroscopy

Figure S15. UV-Vis spectra of $[\text{Cu}(\mu\text{-Pip})(\mu\text{-Ac})(\text{MeOH})]_2$ (**1**), $[\text{Cu}(\text{Pip})_2(\text{py})_2(\text{H}_2\text{O})]$ (**2**), $[\text{Cu}(\text{Pip})_2(3\text{-Phpy})_2(\text{H}_2\text{O})]$ (**3**), $[\text{Cu}(\text{Pip})_2(4\text{-Acpy})_2(\text{H}_2\text{O})]$ (**4**), $[\text{Cu}(\text{Pip})_2(3,5\text{-dmpz})_2]$ (**5**), $[\text{Cu}(\text{Pip})_2(\text{DMF})_2]_2 \cdot 2\text{DMF}$ (**6**) and $[\text{Cu}(\text{Pip})_2(2\text{-Bzpy})]_2$ (**7**) in MeOH (**1–5**, **7**) or DMF:MeOH (1:2.5) (**6**) (aprox. $1 \cdot 10^{-3}$ M) at room temperature.

X-ray crystal structures

For **2**, the integration of the data using a monoclinic unit cell yielded a total of 8490 reflections to a maximum θ angle of 24.45° (0.86 Å resolution), of which 1954 were independent (average redundancy 4345, completeness = 99.1%, R_{int} = 4.49%, R_{sig} = 3.88%) and 1752 (89.66%) were greater than 2σ (F^2). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6333 and 0.7451. For **3**, the integration of the data using a monoclinic unit cell yielded a total of 32090 reflections to a maximum θ angle of 27.52° (0.77 Å resolution), of which 3576 were independent (average redundancy 8974, completeness = 99.5%, R_{int} = 13.65%, R_{sig} = 6.00%) and 2633 (73.63%) were greater than $2\sigma(F^2)$. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6731 and 0.7456. For **4**, the integration of the data using a monoclinic unit cell yielded a total of 51462 reflections to a maximum θ angle of 21.48° (0.97 Å resolution), of which 1898 were independent (average redundancy 27114, completeness = 99.6%, R_{int} = 6.91%, R_{sig} = 1.68%) and 1728 (91.04%) were greater than $2\sigma(F^2)$. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6930 and 0.7446. For **5**, the integration of the data using a triclinic unit cell yielded a total of 29716 reflections to a maximum θ angle of 26.73° (0.79 Å resolution), of which 5397 were independent (average redundancy 5506, completeness = 99.6%, R_{int} = 3.45%, R_{sig} = 2.37%) and 4560 (84.49%) were greater than 2σ (F^2). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6940 and 0.7454. For **6**, the integration of the data using a triclinic unit cell yielded a total of 46464 reflections to a maximum θ angle of 30.56° (0.70 Å resolution), of which 6939 were independent (average redundancy 6696, completeness = 99.6%, R_{int} = 3.05%, R_{sig} = 2.16%) and 6069 (87.46%) were greater than $2\sigma(F^2)$. The calculated minimum and maximum transmission coefficients (based on crystal size)

are 0.6897 and 0.7461. For **7**, the integration of the data using a monoclinic unit cell yielded a total of 122091 reflections to a maximum θ angle of 28.33° (0.75 Å resolution), of which 11916 were independent (average redundancy 10246, completeness = 99.4%, $R_{\text{int}} = 4.95\%$, $R_{\text{sig}} = 2.36\%$) and 9844 (82.61%) were greater than $2\sigma(F^2)$. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6985 and 0.7457.

The structures were solved using the Bruker SHELXTL Software, package and refined using SHELX [1]. For **2**, the final anisotropic full-matrix least-squares refinement on F^2 with 159 variables converged at $R_1 = 8.30\%$, for the observed data and $wR_2 = 22.72\%$ for all data. For **3**, the final anisotropic full-matrix least-squares refinement on F^2 with 230 variables converged at $R_1 = 5.17\%$, for the observed data and $wR_2 = 10.74\%$ for all data. For **4**, the final anisotropic full-matrix least-squares refinement on F^2 with 222 variables converged at $R_1 = 6.75\%$, for the observed data and $wR_2 = 18.12\%$ for all data. For **5**, the final anisotropic full-matrix least-squares refinement on F^2 with 359 variables converged at $R_1 = 2.93\%$, for the observed data and $wR_2 = 7.61\%$ for all data. For **6**, the final anisotropic full-matrix least-squares refinement on F^2 with 317 variables converged at $R_1 = 4.27\%$, for the observed data and $wR_2 = 11.19\%$ for all data. For **7**, the final anisotropic full-matrix least-squares refinement on F^2 with 685 variables converged at $R_1 = 3.59\%$, for the observed data and $wR_2 = 9.76\%$ for all data.

References

[1] G.M. Sheldrick, Acta Cryst. 2015, C71, 3-8.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) mo_c20vb25_0m_aa

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: mo_c20vb25_0m_aa

Bond precision: C-C = 0.0128 Å Wavelength=0.71073

Cell: a=15.530(3) b=6.1225(12) c=25.132(5)
 alpha=90 beta=91.533(6) gamma=90

Temperature: 100 K

	Calculated	Reported
Volume	2388.8(8)	2388.7(8)
Space group	C 2/c	C 2/c
Hall group	: -C 2yc	-C 2yc
Moiety formula	C26 H22 Cu N2 O9	C26 H22 Cu N2 O9
Sum formula	C26 H22 Cu N2 O9	C26 H22 Cu N2 O9
Mr	570.01	569.99
Dx,g cm-3	1.585	1.585
Z	4	4
Mu (mm-1)	0.975	0.975
F000	1172.0	1172.0
F000'	1173.86	
h,k,lmax	18,7,29	18,7,29
Nref	1970	1953
Tmin,Tmax	0.929,0.941	0.633,0.745
Tmin'	0.749	

Correction method= # Reported T Limits: Tmin=0.633 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.991 Theta(max)= 24.446

R(reflections)= 0.0853(1751) wR2(reflections)= 0.2320(1953)

S = 1.117 Npar= 135

The following ALERTS were generated. Each ALERT has the format

test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

● Alert level C

DIFMX02_ALERT_1_C The maximum difference density is > 0.1*ZMAX*0.75
The relevant atom site should be identified.

THETM01_ALERT_3_C The value of $\sin(\theta_{\max})/\lambda$ is less than 0.590
Calculated $\sin(\theta_{\max})/\lambda = 0.5823$

PLAT097_ALERT_2_C Large Reported Max. (Positive) Residual Density 2.32 eA-3

PLAT220_ALERT_2_C Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range 3.4 Ratio

PLAT220_ALERT_2_C Non-Solvent Resd 1 O Ueq(max)/Ueq(min) Range 4.3 Ratio

PLAT222_ALERT_3_C Non-Solv. Resd 1 H Uiso(max)/Uiso(min) Range 6.3 Ratio

PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X) Cu1 --N1 . 5.2 s.u.

PLAT234_ALERT_4_C Large Hirshfeld Difference O3 --C14 0.18 Ang.

PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of 04 Check

PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor 2.2 Note

PLAT334_ALERT_2_C Small Aver. Benzene C-C Dist C7 -C12 1.37 Ang.

PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds 0.01282 Ang.

PLAT906_ALERT_3_C Large K Value in the Analysis of Variance 3.568 Check

PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.582 15 Report

PLAT971_ALERT_2_C Check Calcd Resid. Dens. 0.11A From C7 2.50 eA-3

PLAT971_ALERT_2_C Check Calcd Resid. Dens. 1.06A From Cu1 2.07 eA-3

PLAT971_ALERT_2_C Check Calcd Resid. Dens. 0.04A From N1 1.71 eA-3

PLAT972_ALERT_2_C Check Calcd Resid. Dens. 0.10A From C9 -1.87 eA-3

PLAT977_ALERT_2_C Check Negative Difference Density on H4 -0.40 eA-3

PLAT978_ALERT_2_C Number C-C Bonds with Positive Residual Density. 0 Info

● Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 2 Note

PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 78.16 Why ?

PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records 2 Report

PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records 1 Report

PLAT398_ALERT_2_G Deviating C-O-C Angle From 120 for O3 106.2 Degree

PLAT398_ALERT_2_G Deviating C-O-C Angle From 120 for O4 108.1 Degree

PLAT794_ALERT_5_G Tentative Bond Valency for Cu1 (II) . 2.16 Info

PLAT860_ALERT_3_G Number of Least-Squares Restraints 1 Note

PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still 75% Note

PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min). 2 Note

PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF 1 Note

PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ... 1 Note

PLAT955_ALERT_1_G Reported (CIF) and Actual (FCF) Lmax Differ by . 1 Units

0 **ALERT level A** = Most likely a serious problem - resolve or explain

0 **ALERT level B** = A potentially serious problem, consider carefully

20 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight

13 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

18 ALERT type 2 Indicator that the structure model may be wrong or deficient

9 ALERT type 3 Indicator that the structure quality may be low

3 ALERT type 4 Improvement, methodology, query or suggestion

1 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) mo_C20VB71A_0ma_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: mo_C20VB71A_0ma_a

Bond precision:	C-C = 0.0047 Å	Wavelength=0.71073
Cell:	a=22.6648(13)	b=5.7527(3) c=23.9870(16)
	alpha=90	beta=95.958(4) gamma=90
Temperature:	100 K	
	Calculated	Reported
Volume	3110.6(3)	3110.6(3)
Space group	C 2/c	C 2/c
Hall group	: -C 2yc	-C 2yc
Moiety formula	C38 H30 Cu N2 O9	C38 H30 Cu N2 O9
Sum formula	C38 H30 Cu N2 O9	C38 H30 Cu N2 O9
Mr	722.19	722.18
Dx,g cm-3	1.542	1.542
Z	4	4
Mu (mm-1)	0.767	0.767
F000	1492.0	1492.0
F000'	1493.97	
h,k,lmax	29,7,31	29,7,31
Nref	3592	3576
Tmin,Tmax	0.911,0.971	0.673,0.746
Tmin'	0.581	

Correction method= # Reported T Limits: Tmin=0.673 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.996 Theta(max)= 27.518

R(reflections)= 0.0518(2633) wR2(reflections)= 0.1073(3576)

S = 1.056 Npar= 230

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

● **Alert level C**

RINTA01_ALERT_3_C The value of Rint is greater than 0.12

Rint given 0.137

PLAT906_ALERT_3_C Large K Value in the Analysis of Variance 3.051 Check

● **Alert level G**

PLAT002_ALERT_2_G	Number of Distance or Angle Restraints on AtSite	2	Note
PLAT020_ALERT_3_G	The Value of Rint is Greater Than 0.12	0.137	Report
PLAT063_ALERT_4_G	Crystal Size Likely too Large for Beam Size	0.71	mm
PLAT083_ALERT_2_G	SHELXL Second Parameter in WGHT Unusually Large	14.96	Why ?
PLAT172_ALERT_4_G	The CIF-Embedded .res File Contains DFIX Records	1	Report
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O3	104.6	Degree
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O4	103.7	Degree
PLAT794_ALERT_5_G	Tentative Bond Valency for Cu1 (II) .	2.18	Info
PLAT860_ALERT_3_G	Number of Least-Squares Restraints	1	Note
PLAT910_ALERT_3_G	Missing # of FCF Reflection(s) Below Theta(Min).	2	Note
PLAT912_ALERT_4_G	Missing # of FCF Reflections Above STh/L= 0.600	15	Note
PLAT955_ALERT_1_G	Reported (CIF) and Actual (FCF) Lmax Differ by .	1	Units
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	2	Info

- 0 **ALERT level A** = Most likely a serious problem - resolve or explain
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13 **ALERT level G** = General information/check it is not something unexpected

- 1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
5 ALERT type 2 Indicator that the structure model may be wrong or deficient
5 ALERT type 3 Indicator that the structure quality may be low
3 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check
-
-

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Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) mo_C20VB192_0m_a

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: mo_C20VB192_0m_a

Bond precision:	C-C = 0.0102 Å	Wavelength=0.71073
Cell:	a=23.1610(17)	b=5.8928(4) c=26.0634(19)
	alpha=90	beta=110.439(2) gamma=90
Temperature:	100 K	
	Calculated	Reported
Volume	3333.3(4)	3333.3(4)
Space group	C 2/c	C 2/c
Hall group	-C 2yc	-C 2yc
Moiety formula	C30 H26 Cu N2 O11, C2 H3 O2, C O, O	?
Sum formula	C33 H29 Cu N2 O15	C33 H36 Cu N2 O15
Mr	757.13	764.18
Dx,g cm-3	1.509	1.523
Z	4	4
Mu (mm-1)	0.733	0.733
F000	1560.0	1588.0
F000'	1562.16	
h,k,lmax	23,6,26	23,6,26
Nref	1904	1898
Tmin,Tmax	0.942,0.977	0.693,0.745
Tmin'	0.877	

Correction method= # Reported T Limits: Tmin=0.693 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.997 Theta(max)= 21.480

R(reflections)= 0.0675(1728) wR2(reflections)= 0.1812(1898)

S = 1.084 Npar= 222

The following ALERTS were generated. Each ALERT has the format

test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

Alert level A

THETM01_ALERT_3_A The value of $\sin(\theta_{\max})/\lambda$ is less than 0.550
Calculated $\sin(\theta_{\max})/\lambda = 0.5152$

Alert level C

REFNR01_ALERT_3_C Ratio of reflections to parameters is < 10 for a centrosymmetric structure
 $\sin(\theta)/\lambda$ 0.5152
Proportion of unique data used 1.0000
Ratio reflections to parameters 8.5495

PLAT018_ALERT_1_C $\text{_diffn_measured_fraction_theta_max}$.NE. *_full ! Check
PLAT041_ALERT_1_C Calc. and Reported SumFormula Strings Differ Please Check
PLAT043_ALERT_1_C Calculated and Reported Mol. Weight Differ by .. 7.05 Check
PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)... Please Check
PLAT088_ALERT_3_C Poor Data / Parameter Ratio 8.55 Note
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density 2.13 Report
PLAT213_ALERT_2_C Atom O5W has ADP max/min Ratio 4.0 prolat
PLAT220_ALERT_2_C Non-Solvent Resd 1 C $U_{eq}(\max)/U_{eq}(\min)$ Range 4.5 Ratio
PLAT220_ALERT_2_C Non-Solvent Resd 1 O $U_{eq}(\max)/U_{eq}(\min)$ Range 5.0 Ratio
PLAT222_ALERT_3_C Non-Solv. Resd 1 H $U_{iso}(\max)/U_{iso}(\min)$ Range 4.9 Ratio
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average $U(i,j)$ Tensor 2.4 Note
PLAT309_ALERT_2_C Single Bonded Oxygen (C-O > 1.3 Ang) C1W Check
PLAT309_ALERT_2_C Single Bonded Oxygen (C-O > 1.3 Ang) O3W Check
PLAT309_ALERT_2_C Single Bonded Oxygen (C-O > 1.3 Ang) O4W Check
PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds 0.01015 Ang.
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.515 4 Report
PLAT939_ALERT_3_C Large Value of Not (SHELXL) Weight Optimized S . 10.12 Check
PLAT971_ALERT_2_C Check Calcd Resid. Dens. 1.14A From C3W 1.61 eA-3

Alert level G

FORMU01_ALERT_2_G There is a discrepancy between the atom counts in the $\text{_chemical_formula_sum}$ and the formula from the _atom_site* data.
Atom count from $\text{_chemical_formula_sum}$: C33 H36 Cu1 N2 O15
Atom count from the _atom_site data: C33 H29 Cu1 N2 O15

CELLZ01_ALERT_1_G Difference between formula and atom_site contents detected.
CELLZ01_ALERT_1_G WARNING: H atoms missing from atom site list. Is this intentional?
From the CIF: $\text{_cell_formula_units_Z}$ 4
From the CIF: $\text{_chemical_formula_sum}$ C33 H36 Cu N2 O15
TEST: Compare cell contents of formula and atom_site data

atom	Z*formula	cif sites	diff
C	132.00	132.00	0.00
H	144.00	116.00	28.00
Cu	4.00	4.00	0.00
N	8.00	8.00	0.00
O	60.00	60.00	0.00

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 8 Note
PLAT017_ALERT_1_G Check Scattering Type Consistency of C1W as O
PLAT017_ALERT_1_G Check Scattering Type Consistency of O1W as C
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 52.39 Why ?
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records 4 Report
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records 5 Report
PLAT300_ALERT_4_G Atom Site Occupancy of C1W Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of O3W Constrained at 0.5 Check

PLAT300_ALERT_4_G	Atom Site Occupancy of C3W	Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H3WA	Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H3WB	Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of H3WC	Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of O4W	Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of C4W	Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of O2W	Constrained at	0.5	Check
PLAT302_ALERT_4_G	Anion/Solvent/Minor-Residue Disorder (Resd 2)		75%	Note
PLAT302_ALERT_4_G	Anion/Solvent/Minor-Residue Disorder (Resd 3)		100%	Note
PLAT302_ALERT_4_G	Anion/Solvent/Minor-Residue Disorder (Resd 4)		100%	Note
PLAT304_ALERT_4_G	Non-Integer Number of Atoms in Resd 4		0.50	Check
PLAT311_ALERT_2_G	Isolated Disordered Oxygen Atom (No H's ?)		O2W	Check
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O3		104.2	Degree
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O4		104.2	Degree
PLAT720_ALERT_4_G	Number of Unusual/Non-Standard Labels		5	Note
PLAT794_ALERT_5_G	Tentative Bond Valency for Cu1 (II) .		2.18	Info
PLAT802_ALERT_4_G	CIF Input Record(s) with more than 80 Characters		1	Info
PLAT860_ALERT_3_G	Number of Least-Squares Restraints		5	Note
PLAT909_ALERT_3_G	Percentage of I>2sig(I) Data at Theta(Max) Still		33%	Note
PLAT910_ALERT_3_G	Missing # of FCF Reflection(s) Below Theta(Min).		3	Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.		1	Info

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checkCIF/PLATON report

Structure factors have been supplied for datablock(s) mo_C20VB195_0m_a

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: mo_C20VB195_0m_a

Bond precision:	C-C = 0.0030 A	Wavelength=0.71073
Cell:	a=6.0789(2)	b=12.4827(4) c=17.7198(6)
	alpha=73.049(1)	beta=83.955(1) gamma=86.468(2)
Temperature:	100 K	
	Calculated	Reported
Volume	1278.35(7)	1278.35(7)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C26 H26 Cu N4 O8	C26 H26 Cu N4 O8
Sum formula	C26 H26 Cu N4 O8	C26 H26 Cu N4 O8
Mr	586.06	586.05
Dx,g cm-3	1.523	1.523
Z	2	2
Mu (mm-1)	0.913	0.913
F000	606.0	606.0
F000'	606.91	
h,k,lmax	7,15,22	7,15,22
Nref	5420	5397
Tmin,Tmax	0.860,0.929	0.694,0.745
Tmin'	0.806	

Correction method= # Reported T Limits: Tmin=0.694 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.996 Theta(max)= 26.728

R(reflections)= 0.0293(4560) wR2(reflections)= 0.0761(5397)

S = 1.020 Npar= 359

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.600

12 Report

Alert level G

PLAT007_ALERT_5_G	Number of Unrefined Donor-H Atoms	2	Report
PLAT398_ALERT_2_G	Deviating C-O-C Angle from 120 Deg for O3A	105.1	Degree
PLAT398_ALERT_2_G	Deviating C-O-C Angle from 120 Deg for O4A	104.7	Degree
PLAT398_ALERT_2_G	Deviating C-O-C Angle from 120 Deg for O3B	105.8	Degree
PLAT398_ALERT_2_G	Deviating C-O-C Angle from 120 Deg for O4B	105.7	Degree
PLAT720_ALERT_4_G	Number of Unusual/Non-Standard Labels	4	Note
PLAT794_ALERT_5_G	Tentative Bond Valency for Cu1A (II)	2.18	Info
PLAT794_ALERT_5_G	Tentative Bond Valency for Cu1B (II)	2.34	Info
PLAT910_ALERT_3_G	Missing # of FCF Reflection(s) Below Theta(Min).	4	Note
PLAT912_ALERT_4_G	Missing # of FCF Reflections Above STh/L= 0.600	7	Note
PLAT913_ALERT_3_G	Missing # of Very Strong Reflections in FCF	1	Note
PLAT933_ALERT_2_G	Number of OMIT Records in Embedded .res File ...	1	Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	15	Info

0 **ALERT level A** = Most likely a serious problem - resolve or explain

0 **ALERT level B** = A potentially serious problem, consider carefully

1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight

13 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

6 ALERT type 2 Indicator that the structure model may be wrong or deficient

3 ALERT type 3 Indicator that the structure quality may be low

2 ALERT type 4 Improvement, methodology, query or suggestion

3 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

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Publication of your CIF in other journals

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checkCIF/PLATON report

Structure factors have been supplied for datablock(s) mo_C20VB106_0m_a

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: mo_C20VB106_0m_a

Bond precision: C-C = 0.0031 A

Wavelength=0.71073

Cell: a=10.4359(5) b=11.1697(5) c=12.1119(6)
 alpha=87.276(2) beta=65.220(2) gamma=64.078(2)
Temperature: 100 K

	Calculated	Reported
Volume	1136.84(10)	1136.84(10)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C38 H34 Cu2 N2 O18, 2(C3 H7 N O)	C38 H34 Cu2 N2 O18, 2(C3 H7 N O)
Sum formula	C44 H48 Cu2 N4 O20	C44 H48 Cu2 N4 O20
Mr	1079.96	1079.94
Dx,g cm-3	1.577	1.577
Z	1	1
Mu (mm-1)	1.023	1.023
F000	558.0	558.0
F000'	558.93	
h,k,lmax	14,15,17	14,15,17
Nref	6963	6937
Tmin,Tmax	0.824,0.853	0.690,0.746
Tmin'	0.788	

Correction method= # Reported T Limits: Tmin=0.690 Tmax=0.746

AbsCorr = MULTI-SCAN

Data completeness= 0.996

Theta(max)= 30.557

R(reflections)= 0.0427(6068)

wR2(reflections)= 0.1119(6937)

S = 1.036

Npar= 317

The following ALERTS were generated. Each ALERT has the format

test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

Alert level C

PLAT220_ALERT_2_C	Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range	3.6	Ratio
PLAT244_ALERT_4_C	Low 'Solvent' Ueq as Compared to Neighbors of	N2	Check
PLAT250_ALERT_2_C	Large U3/U1 Ratio for Average U(i,j) Tensor	2.8	Note
PLAT309_ALERT_2_C	Single Bonded Oxygen (C-O > 1.3 Ang)	010'	Check
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.600	10	Report
PLAT913_ALERT_3_C	Missing # of Very Strong Reflections in FCF	4	Note

Alert level G

PLAT154_ALERT_1_G	The s.u.'s on the Cell Angles are Equal ..(Note)	0.002	Degree
PLAT171_ALERT_4_G	The CIF-Embedded .res File Contains EADP Records	2	Report
PLAT300_ALERT_4_G	Atom Site Occupancy of O10 Constrained at	0.5	Check
PLAT300_ALERT_4_G	Atom Site Occupancy of O10' Constrained at	0.5	Check
PLAT302_ALERT_4_G	Anion/Solvent/Minor-Residue Disorder (Resd 2)	20%	Note
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O3	106.5	Degree
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O4	105.0	Degree
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O7	106.1	Degree
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O8	106.2	Degree
PLAT794_ALERT_5_G	Tentative Bond Valency for Cu1 (II) .	2.11	Info
PLAT910_ALERT_3_G	Missing # of FCF Reflection(s) Below Theta(Min).	4	Note
PLAT912_ALERT_4_G	Missing # of FCF Reflections Above STh/L= 0.600	12	Note
PLAT933_ALERT_2_G	Number of OMIT Records in Embedded .res File ...	2	Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	8	Info

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checkCIF/PLATON report

Structure factors have been supplied for datablock(s) mo_C20VB206_0ma_a

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: mo_C20VB206_0ma_a

Bond precision: C-C = 0.0031 A Wavelength=0.71073

Cell: a=17.0709(6) b=18.5452(7) c=15.3980(5)
 alpha=90 beta=99.832(1) gamma=90

Temperature: 100 K

	Calculated	Reported
Volume	4803.2(3)	4803.2(3)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C56 H42 Cu2 N2 O16	C56 H42 Cu2 N2 O16
Sum formula	C56 H42 Cu2 N2 O16	C56 H42 Cu2 N2 O16
Mr	1126.02	1125.99
Dx,g cm-3	1.557	1.557
Z	4	4
Mu (mm-1)	0.965	0.965
F000	2312.0	2312.0
F000'	2315.67	
h,k,lmax	22,24,20	22,24,20
Nref	11989	11916
Tmin,Tmax	0.909,0.958	0.698,0.746
Tmin'	0.765	

Correction method= # Reported T Limits: Tmin=0.698 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.994 Theta(max)= 28.332

R(reflections)= 0.0359(9844) wR2(reflections)= 0.0976(11916)

S = 1.048 Npar= 685

The following ALERTS were generated. Each ALERT has the format

test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

● Alert level C

PLAT220_ALERT_2_C	Non-Solvent Resd 1 0 Ueq(max)/Ueq(min) Range	3.2 Ratio
PLAT241_ALERT_2_C	High 'MainMol' Ueq as Compared to Neighbors of	03 Check
PLAT241_ALERT_2_C	High 'MainMol' Ueq as Compared to Neighbors of	04 Check
PLAT241_ALERT_2_C	High 'MainMol' Ueq as Compared to Neighbors of	C18 Check
PLAT910_ALERT_3_C	Missing # of FCF Reflection(s) Below Theta(Min).	6 Note
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.600	49 Report
PLAT934_ALERT_3_C	Number of (Iobs-Icalc)/SigmaW > 10 Outliers	1 Check

● Alert level G

PLAT003_ALERT_2_G	Number of Uiso or Uij Restrained non-H Atoms ...	2 Report
PLAT083_ALERT_2_G	SHELXL Second Parameter in WGHT Unusually Large	5.02 Why ?
PLAT177_ALERT_4_G	The CIF-Embedded .res File Contains DELU Records	1 Report
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O3	105.8 Degree
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O4	105.2 Degree
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O7	105.3 Degree
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O8	104.6 Degree
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O11	105.1 Degree
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O12	105.1 Degree
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O15	105.1 Degree
PLAT398_ALERT_2_G	Deviating C-O-C Angle From 120 for O16	105.3 Degree
PLAT860_ALERT_3_G	Number of Least-Squares Restraints	1 Note
PLAT912_ALERT_4_G	Missing # of FCF Reflections Above STh/L= 0.600	18 Note
PLAT913_ALERT_3_G	Missing # of Very Strong Reflections in FCF	3 Note
PLAT933_ALERT_2_G	Number of OMIT Records in Embedded .res File ...	8 Note
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	12 Info

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-
-

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