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# Synthesis of Cu(II) and Mn(III) Complexes Involving Derivatives of Pyridine[1]

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**Abstract**—Two complexes with derivatives of pyridine as ligands were synthesized and characterized. From the reaction of 2-pyridinecarboxaldehyde oxime with $Cu(OAc)_2 \cdot H_2O$ afforded the complex $C_{20}H_{30}N_6O_{12}Cu_3$ (**I**), and the use of 3-hydroxy-2-pyridinecarboxylic acid with anhydrous $MnCl_2 \cdot 4H_2O$ led to the formation of another complex $C_{12}H_{14}N_2OCl_2Mn$ (**II**). They were characterized by X-ray diffraction (CIF files CCDC nos. 568718 (**I**) and 1568880 (**II**)), NMR, IR and elemental analysis. For **I**: terigonal, space group $R\bar{3}/H$, $a$ = 42.548(3), $c$ = 10.2774(9) Å, $V$ = 16113(2) Å$^3$, $Z$ = 18, $\rho_{calcd}$ = 1.367 Mg/m$^3$, the final $R$ factor was $R_1$ = 0.0945, 6662 for reflections were observed with $I > 2\sigma(I)$, $wR$ = 0.162 for all data. For **II**: triclinic, $P\bar{1}$, $a$ = 5.6174(9), $b$ = 7.7259(13), $c$ = 9.7160(16) Å, $\alpha$ = 70.444(3)°, $\beta$ = 88.009(3)°, $\gamma$ = 89.818(3)°, $V$ = 397.09(11) Å$^3$, $Z$ = 1, $\rho_{calcd}$ = 1.840 Mg/m$^3$, the final $R$ factor was $R_1$ = 0.0281, 4280 for reflections were observed with $I > 2\sigma(I)$, $wR$ = 0.0775 for all data.

*Keywords:* 2-pyridinecarboxaldehyde oxime, 3-hydroxy-2-pyridine carboxylic acid, metal salts

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## INTRODUCTION

Cu(II) and Mn(II) metal complexes with Schiff base ligands have received considerable recent attention due to their important biological activities, such as their antifungal, antibacterial, antimalarial, antitumor, antiproliferative, anti-inflammatory, antiviral, antioxidant and antipyretic properties [1–3]. It is well-known that O and N donor Schiff bases are usually used as chelating ligands for the synthesis of organometallic complexes [4–7], for example, the synthesis of $Mn[C_{27}H_{21}N_3O_4] \cdot H_2O$ [8], $Mn(C_{29}H_{24}N_2O_4)(CH_3COO)(H_2O)_2$ [9], $C_{25}H_{31}MnN_2O$ [10], $C_{16}H_{37.50}N_{6.50}S_3Cu_3Cl$ [11], and $Cu_3OL_3(ClO_4)]H_2O$ [12]. These complexes have shown good catalytic activity for the reaction of ethyl pyruvate and nitromethane [13–18].

In this paper, we report the first synthesis of the complexes $C_{20}H_{30}N_6O_{12}Cu_3$ (**I**) and $C_{12}H_{14}N_2O_8Cl_2Mn$ (**II**) by a direct one-pot method.

## EXPERIMENTAL

**Materials and methods.** All reagents and raw materials were used without any purification or processing. $Cu(OAc)_2 \cdot H_2O$ and $Mn(OAc)_2 \cdot 4H_2O$ were purchased from the Sinopharm Chemical Reagent Company. 2-Pyridinecarboxaldehyde oxime and 3-hydroxy-2-pyridinecarboxylic acid were purchased from J&K Scientific LTD. $^1$H NMR spectra were obtained using a Bruker AM-600 spectrometer, and the crystal structures were determined using a Gemini S Ultra diffractometer. Infrared spectra were recorded on a Mattson Galaxy Series FTIR 3000 spectrometer; the peaks are reported in cm$^{-1}$. Elemental analysis was performed using a VARIO ELIII elemental analyzer. The crystal structure was determined using a Gemini S Ultra diffractometer.

**Synthesis of complex I.** 2-Pyridine formaldehyde oxime (1.1946 g, 9.78 mmol) was added to a 100-mL round-bottom flask that was charged with anhydrous methanol and stirred to dissolve. Then $Cu(OAc)_2 \cdot H_2O$ (1.9908 g, 9.97 mmol) was weighed into the above solution. The mixture was refluxed for 36 h and subsequently filtered while hot. The solution was evaporated slowly in air and brown crystals were obtained that were suitable for X-ray single-crystal analysis. The yield was 42.6%; m.p. = 126–130°C.

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[1] The article is published in the original..

#C. C. Guo, L. Qi contribute equally to this research work.

The crystal structure was determined by X-ray diffraction.

For $C_{20}H_{30}N_6O_{12}Cu_3$ (**I**)

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 32.59 | H, 4.10 | N, 11.40 |
| Found, % | C, 33.10 | H, 4.29 | N, 10.38 |

IR (KBr; ν, $cm^{-1}$): 3455, 3053, 3412, 3230, 3135, 1569, 1503, 1401, 740, 681.

**Synthesis of complex II.** 3-Hydroxy-2-pyridinecarboxylate (0.1368 g, 1.44 mmol) and manganese chloride tetrahydrate (0.5692 g, 2.88 mmol) were dissolved in anhydrous methanol (40 mL) and the mixture was refluxed for 48 h. After hot filtration, the solution was evaporated slowly in air and dark green crystals were obtained that were suitable for X-ray single-crystal analysis. The yield was 30%; m.p. = 180–182°C.

IR (KBr; ν, $cm^{-1}$): 3984, 3737, 3329, 1794, 1634, 1510, 1459, 1430, 1336, 1277, 979, 833, 737, 659, 564.

For $C_{12}H_{14}N_2O_8Cl_2Mn$ (**II**)

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 32.75 | H, 3.38 | N, 6.37 |
| Found, % | C, 32.17 | H, 3.58 | N, 5.98 |

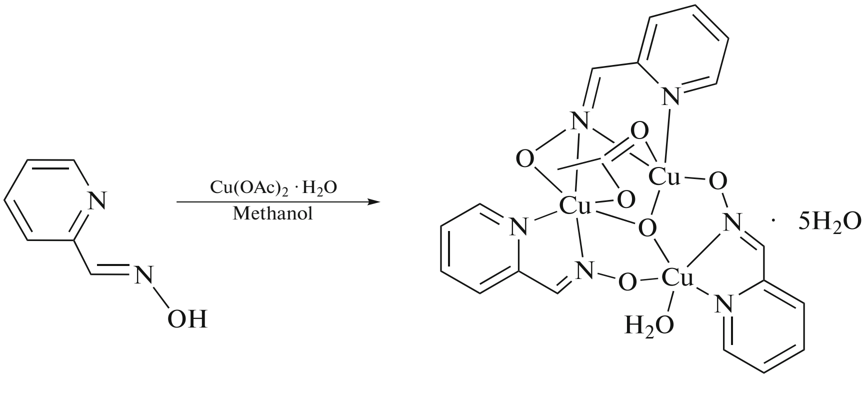
**X-ray structure determination.** A green crystal of compound **I** with approximate dimensions of 0.180 × 0.140 × 0.110 mm was selected for data collection on a BRUKER SMART diffractometer with graphite-monochromated Mo$K_\alpha$ radiation ($\lambda = 0.71073$ Å). A total of 7130 reflections were collected in a range of $0.951° < \theta < 25.491°$ by using ω–φ scan techniques at 293(2) K, $M = 737.12$, in a trigonal space group. $R\bar{3}/H$, $a = 42.548(3)$, $c = 10.2774(9)$ Å, $V = 16113(2)$ Å$^3$, $Z = 18$, $\rho_{calcd} = 1.367$ Mg/m$^3$, and the final $R$ factor was $R_1 = 0.0945$, 6662 for reflections that were observed with $I > 2\sigma(I)$, $wR = 0.1622$ for all the data. The structure was solved by full-matrix least-squares on $F^2$ using the SHELXTL program. All the non-H atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were located theoretically and refined with riding model position parameters and fixed isotropic thermal parameters.

A yellow crystal of compound **II** with approximate dimensions of 0.200 × 0.160 × 0.130 mm was selected for data collection using a BRUKER SMART diffractometer with graphite-monochromated Mo$K_\alpha$ radiation ($\lambda = 0.71073$ Å). A total of 7130 reflections were collected in a range of $2.226° < \theta < 25.996°$ by using ω–φ scan techniques at 293.(2) K, $M = 40.09$, in the monoclinic space group $P\bar{1}$, $a = 5.6174(9)$, $b = 7.7259(13)$, $c = 9.7160(16)$ Å, $\alpha = 70.444(3)°$, $\beta = 88.009(3)°$, $\gamma = 89.818(3)°$, $V = 397.09(11)$ Å$^3$, $Z = 1$, $\rho_{calcd} = 1.840$ Mg/m$^3$, and the final $R$ factor was $R_1 = 0.0281$, 4280 for reflections that were observed with $I > 2\sigma(I)$, $wR = 0.0775$ for all the data. The structure was solved by full-matrix least-squares on $F^2$ using the SHELXTL program. All the non-H atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were located theoretically and refined with riding model position parameters and fixed isotropic thermal parameters. Selected bond lengths, bond angles and hydrogen bonds for complexes **I** and **II** are listed in Tables 1 and 2, respectively.

Supplementary material for structures has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 568718 (**I**) and 1568880 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

## RESULTS AND DISCUSSION

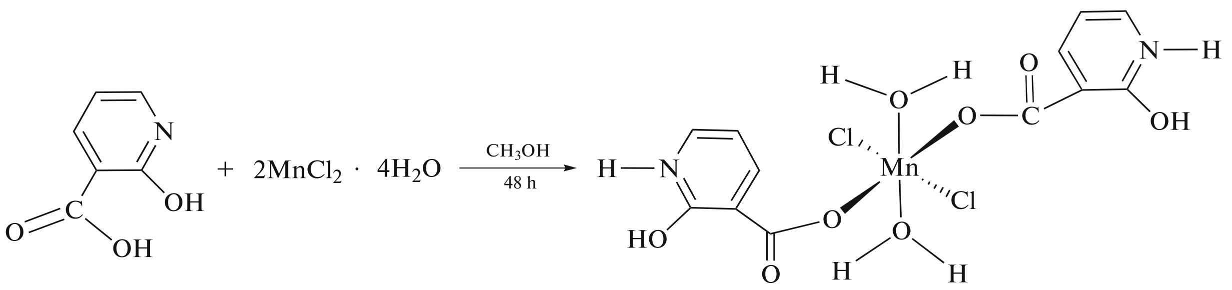
The synthetic route of the complexes **I** and **II** can be summarized as follows:



(**I**)

**Table 1.** Selected bond lengths (Å) and bond angels (deg) for **I**, **II**

| Bond | *d*, Å | Bond | *d*, Å |
|---|---|---|---|
| **I** | | | |
| Cu(1)–O(3) | 1.963(3) | Cu(1)–N(2) | 1.981(4) |
| Cu(1)–O(4) | 1.993(3) | Cu(1)–N(1) | 1.999(5) |
| Cu(1)–O(5) | 2.121(4) | Cu(2)–O(4) | 1.950(3) |
| Cu(2)–O(1) | 1.953(4) | Cu(2)–N(4) | 1.987(5) |
| Cu(2)–N(3) | 1.990(5) | Cu(2)–O(7) | 2.307(4) |
| Cu(3)–O(2) | 1.937(4) | Cu(3)–N(6) | 1.968(4) |
| Cu(3)–O(4) | 1.976(3) | Cu(3)–N(5) | 1.988(4) |
| Cu(3)–O(6) | 2.181(4) | | |
| **II** | | | |
| Mn(1)–O(1) | 2.1433(10) | Mn(1)–Cl(1) | 2.6170(5) |
| Mn(1)–O(4) | 2.1554(12) | | |
| Angle | ω, deg | Angle | ω, deg |
| **I** | | | |
| O(3)Cu(1)N(2) | 170.31(17) | O(3)Cu(1)O(4) | 93.01(14) |
| N(2)Cu(1)O(4) | 87.05(16) | O(3)Cu(1)N(1) | 94.86(17) |
| N(2)Cu(1)N(1) | 81.15(19) | O(4)Cu(1)N(1) | 154.11(16) |
| O(3)Cu(1)O(5) | 97.59(16) | N(2)Cu(1)O(5) | 92.00(18) |
| O(4)Cu(1)O(5) | 97.82(16) | N(1)Cu(1)O(5) | 105.51(17) |
| O(4)Cu(2)O(1) | 93.75(15) | O(4)Cu(2)N(4) | 88.95(17) |
| O(1)Cu(2)N(4) | 164.41(19) | O(4)Cu(2)N(3) | 169.40(19) |
| O(1)Cu(2)N(3) | 95.1(2) | N(4)Cu(2)N(3) | 81.0(2) |
| O(4)Cu(2)O(7) | 86.93(15) | O(1)Cu(2)O(7) | 97.6(2) |
| N(4)Cu(2)O(7) | 97.9(2) | N(3)Cu(2)O(7) | 97.64(17) |
| N(6)Cu(3)O(4) | 88.53(16) | O(2)Cu(3)N(5) | 95.00(19) |
| N(6)Cu(3)N(5) | 81.0(2) | O(4)Cu(3)N(5) | 157.65(17) |
| O(2)Cu(3)O(6) | 93.77(18) | N(6)Cu(3)O(6) | 92.62(17) |
| O(4)Cu(3)O(6) | 96.94(16) | N(5)Cu(3)O(6) | 103.19(17) |
| **II** | | | |
| O(1)$^{\#1}$Mn(1)O(4) | 95.70(5) | O(1)Mn(1)O(4) | 84.30(5) |
| O(1)Mn(1)Cl(1) | 89.34(4) | O(1)$^{\#1}$Mn(1)Cl(1) | 90.66(3) |
| O(4)Mn(1)Cl(1) | 87.84(4) | O(4)$^{\#1}$Mn(1)Cl(1) | 92.16(4) |
| Mn(1)O(4)H(4*A*) | 120.6(2) | C(1)O(1)Mn(1) | 130.04(10) |
| | | Mn(1)O(4) H(4*B*) | 123(2) |



**(II)**

**Table 2.** Hydrogen bond lengths (Å) and bond angles (deg) for **I** and **II***

| D–H···A | Distance, Å | | | Angle DHA, deg |
|---|---|---|---|---|
| | D–H | H···A | D···A | |
| | | **I** | | |
| C(13)–H(13)···O(2) | 0.93 | 2.63 | 3.112(8) | 113 |
| C(8)–H(8)···O(5)$^{\#1}$ | 0.93 | 2.60 | 3.395(9) | 144 |
| C(7)–H(7)···O(1) | 0.93 | 2.65 | 3.140(8) | 113 |
| C(1)–H(1)···O(3) | 0.93 | 2.66 | 3.146(7) | 113 |
| O(11)–H(14*B*)···O(8)$^{\#2}$ | 0.83 | 2.00 | 2.821(12) | 173 |
| O(14)–H(14*B*)···O(8)$^{\#2}$ | 0.82 | 2.01 | 2.780(9) | 157 |
| O(14)–H(14*A*)···O(13) | 0.85 | 2.43 | 3.031(15) | 129 |
| O(12)–H(12*B*)···O(11) | 0.81 | 2.35 | 3.031(15) | 142 |
| O(11)–H(11*A*)···O(12) | 0.83 | 1.97 | 2.711(9) | 148 |
| O(7)–H(7*B*)···O(14)$^{\#3}$ | 0.82 | 2.21 | 2.936(12) | 149 |
| O(7)–H(7*A*)···O(12)$^{\#3}$ | 0.82 | 2.21 | 2.936(12) | 149 |
| O(7)–H(7*A*)···O(12)$^{\#3}$ | 0.83 | 1.97 | 2.711(9) | 148 |
| O(7)–H(7*B*)···O(14)$^{\#3}$ | 0.81 | 2.35 | 3.031(15) | 142 |
| O(11)–H(11*A*)···O(12) | 0.85 | 2.43 | 3.031(15) | 129 |
| O(12)–H(12*B*)···O(11) | 0.82 | 2.01 | 2.780(9) | 157 |
| O(14)–H(14*A*)···O(13) | 0.83 | 2.00 | 2.821(12) | 173 |
| O(14)–H(14*B*)···O(8)$^{\#2}$ | 0.93 | 2.66 | 3.146(7) | 113 |
| C(1)–H(1)···O(3) | 0.93 | 2.65 | 3.140(8) | 113 |
| C(7)–H(7)···O(1) | 0.93 | 2.60 | 3.395(9) | 144 |
| C(8)–H(8)···O(5)$^{\#1}$ | 0.93 | 2.63 | 3.112(8) | 113 |
| | | **II** | | |
| O(3)–H(3)···O(2)$^{\#2}$ | 0.80(3) | 2.46(3) | 2.9339(19) | 119(2) |
| O(3)–H(3)···O(2) | 0.80(3) | 1.85(3) | 2.5596(18) | 147(3) |
| N(1)–H(1)···Cl(1)$^{\#3}$ | 0.87(2) | 2.40(3) | 3.1988(15) | 153(2) |
| O(4)–H(4*B*)···Cl(1)$^{\#3}$ | 0.81(2) | 2.36(2) | 3.1699(14) | 175(3) |
| O(4)–H(4*A*)···O(3)$^{\#4}$ | 0.80(2) | 2.15(2) | 2.8769(18) | 151(2) |
| O(4)–H(4*A*)···O(2)$^{\#1}$ | 0.80(2) | 2.46(2) | 3.0042(18) | 127(2) |
| C(6)–H(6)···Cl(1)$^{\#5}$ | 0.93 | 2.83 | 3.4903(17) | 129 |

* Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x, -y + 2, -z + 1$; $^{\#2}$ $-x + 1, -y + 1, -z + 1$; $^{\#3}$ $x, y - 1, z + 1$ (**I**); $^{\#1}$ $-x + 1, -y, -z$; $^{\#2}$ $-x + 1, -y, -z + 1$; $^{\#3}$ $-x, -y, -z$; $^{\#4}$ $x, y, z - 1$; $^{\#5}$ $x - 1, y + 1, z$ (**II**).

The syntheses of complexes **I** and **II** were performed by refluxing in anhydrous methanol for 48 h with a ligand : metal salt ratio of 1 : 1 for the cupric salt or 1 : 2 for the manganese salt. Brown crystals of complex **I** were obtained after slow evaporation of the filtrate, while dark green crystals of complex **II** were afforded by slow volatilization of a mixture of the filtrate and *n*-hexane over two weeks.

Surprisingly, complex **II** was not formed as a hydrochloride salt after the reaction of 3-hydroxy-2-pyridinecarboxylate with manganese chloride tetrahydrate. Instead, protons from the ligand combined with the nitrogen of the pyridine to form a pyridinium cation. Only manganese(II), not chlorine, is involved in the reaction.

Complex **I** is a trinuclear Cu(II) complex with five free water molecules. Its crystal structure can be seen in Fig. 1. It is easy to see that the three copper(II) centers form a triangular array with an additional central $\mu_3$-oxido bridge and the three copper(II) centers do not have equivalent coordination environments. However, Cu(1), Cu(2) and Cu(3) have similar coordination environments with an $N_2O$ ligand set. For example, the coordinating atoms of Cu(1) are one nitrogen

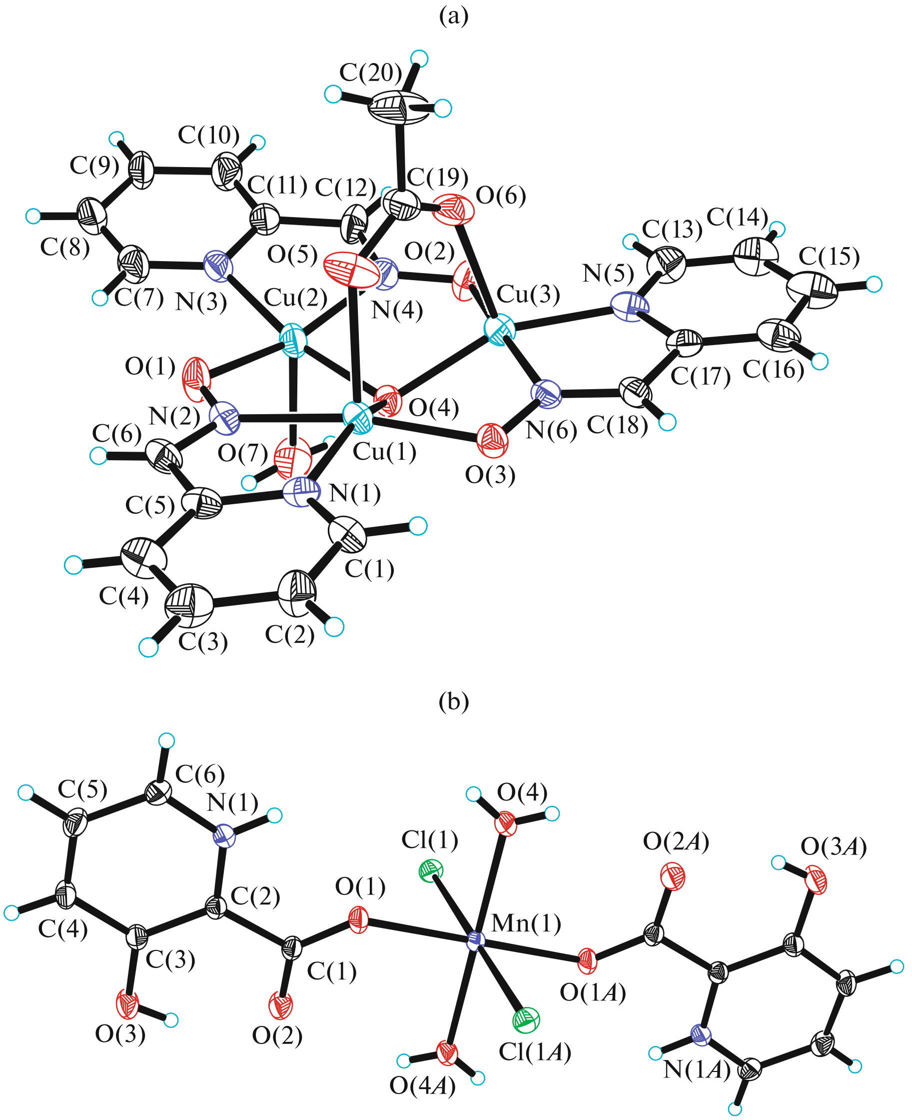


**Fig. 1.** Crystal structure of complexes **I** (a) and **II** (b).

and one oximato oxygen and nitrogen, which is similar to Cu(3), and Cu(1) and Cu(3) are connected via an oxygen bridge from an acetate group. However, the coordinating atoms of Cu(2) also include coordination by one water molecule in addition to one nitrogen, one oximato oxygen and nitrogen and one oxygen atom. The three Cu–N(pyridine) bond distances are Cu(1)–N(1) 1.999(5), Cu(2)–N(3) 1.990(5) and Cu(3)–N(5) 1.988(4) Å. The Cu–N(oxime) bond distances are Cu(1)–N(2) 1.981(4), Cu(2)–N(4) 1.987(5), and Cu(3)–N(6) 1.968(4) Å. The Cu(1)–O(4), Cu(2)–O(4) and Cu(3)–O(4) distances are 1.993, 1.950 and 1.976 Å, respectively. The molecular conformations are stabilized by intramolecular O–H···O hydrogen bonds. In the crystal, the O–H···O interactions lead to long supramolecular chains (Tables 1 and 2).

For complex **II**, the optimized structure of the Mn(II) complex is octahedral. The Mn(II) center adopts a typical octahedral coordination geometry with four oxygen atoms (O(1) and O(1*A*) from two acidic oxygen and O(4) and O(4*A*) from two water molecules) in the ligand and two chloride atoms Cl(1) and Cl(1*A*). The coordination number is six. The length of both Mn–Cl bonds is 2.6170(5) Å. The distance between the Mn–O bonds is 2.1433(10) Å (between the oxygens from the water molecules) and 2.1554(12) Å (between the oxygens from the carboxyl groups). It is worth noting that in this crystal structure, the molecules are linked by weak O–H···O and O–H···Cl hydrogen bonds in a three-dimensional supramolecular architecture. The resulting mononuclear basic unit contains many hydrogen-bonding sites with the –NH and –OH groups acting as hydrogen bond donors and the oxygen atoms acting as hydrogen bond acceptors. Therefore, these basic units could form higher dimensional networks via hydrogen bonding (Tables 1 and 2).

In conclusion, the crystal structures of two complexes $C_{20}H_{30}N_6O_{12}Cu_3$ (**I**) and $C_{12}H_{14}N_2O_8Cl_2Mn$ (**II**) were reported for the first time. Further investigation of their catalytic performance in organic reactions is ongoing, including in the cyanosilylation reaction, the Baylis–Hillman reaction and the silylation reaction.

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