‘Electronic Supplementary Information’

Paramagnetic solid-state NMR assignment and novel chemical conversion of aldehyde group to dihydrogen ortho ester and hemiacetal moieties in copper(II)- and cobalt(II)-pyridinecarboxaldehyde complexes

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Single-crystal X-ray Diffraction Results:

*Cu(II)-4-pyridinecarboxaldehyde (CIF FILE: AC12_100K_2_0m, CCDC 2047187)

Crystal system is trigonal, R-3, unit cell a: 24.4486(3), c: 29.1012(8) Å. 50978 reflections were collected, 6886 independents, Rint: 0.056. The structure was solved using program SHELXS-97 and refined using the full-matrix LS procedure with SHELXL-2014/7. Anisotropic displacement parameters were employed for non-hydrogen atoms. All H atoms were located at the expected positions and they were refined using a riding model. H atoms for water molecule were located in the Fourier difference density map. LS weights of the form \( w = 1/[\sigma^2(F_o^2) + (0.1586 P)^2 + 154.4517 P] \) where \( P = (F_o^2 + 2F_c^2)/3 \), were employed. \( R(F^2) \) = 0.0857, \( wR(F^2) \) = 0.2445. One of the terminal R-CH(OH)(OCH3) hemiacetal group was modeled as two disordered parts (O8C1,O9C,C1C1 and O8C2,O10C,C1C2 as part 1 and 2 respectively) refined with isotropic thermal parameters. Solvent molecules located in channels were also refined with isotropic thermal parameters.
Figure S1. Crystal structure and numbering scheme for the copper complex for the 4-pyridinecarboxaldehyde with CuCl$_2$/CH$_3$OH. The displacement ellipsoids for the non-H atoms in the figure were drawn at the 50% probability level.
Figure S2. Crystal packing structure for the copper complex for the 4-pyridinecarboxaldehyde with CuCl$_2$/CH$_3$OH. The displacement ellipsoids for the non-H atoms in the figure were drawn at the 50% probability level.

Table S1. Crystal data and structure refinement for 4-pyridinecarboxaldehyde with CuCl$_2$/CH$_3$OH (AC12_100K_2_0m)

| Property                     | Value                        |
|------------------------------|------------------------------|
| Identification code          | AC12_100K_2_0m (CCDC 2047187)|
| Empirical formula            | C$_{28}$ H$_{35}$ Cl$_2$ Cu N$_4$ O$_{11}$ |
| Formula weight               | 738.04                       |
| Temperature                  | 100(2) K                     |
| Wavelength                   | 0.71073 Å                    |
Crystal system: Trigonal
Space group: R -3 :H
Unit cell dimensions:
\[ a = 24.4486(3) \text{ Å} \quad \alpha = 90^\circ. \]
\[ b = 24.4486(3) \text{ Å} \quad \beta = 90^\circ. \]
\[ c = 29.1012(8) \text{ Å} \quad \gamma = 120^\circ. \]
Volume: 15064.3(6) Å\(^3\)
Z: 18
Density (calculated): 1.464 Mg/m\(^3\)
Absorption coefficient: 0.874 mm\(^{-1}\)
F(000): 6876
Crystal size: 0.5 x 0.5 x 0.3 mm\(^3\)
Theta range for data collection: 2.099 to 26.423°.
Index ranges: -30 <= h <= 30, -30 <= k <= 30, -36 <= l <= 36
Reflections collected: 50978
Independent reflections: 6886 [R(int) = 0.0562]
Completeness to theta = 25.242°: 99.9 %
Refinement method: Full-matrix least-squares on F\(^2\)
Data / restraints / parameters: 6886 / 0 / 417
Goodness-of-fit on F\(^2\): 1.052
Final R indices [I>2sigma(I)]: R1 = 0.0859, wR2 = 0.2450
R indices (all data): R1 = 0.1076, wR2 = 0.2739
Extinction coefficient: n/a
Largest diff. peak and hole: 1.799 and -1.177 e.Å\(^{-3}\)

**Table S2.** Bond lengths [Å] and angles [°] for 4-pyridinecarboxaldehyde with CuCl2/CH3OH (AC12_100K_2_0m)

| Bond                  | Length (Å)    |
|----------------------|---------------|
| Cu(1)-N(1B)         | 2.018(4)      |
| Cu(1)-N(1D)         | 2.025(4)      |
| Cu(1)-N(1C)         | 2.033(4)      |
| Cu(1)-N(1A)         | 2.038(4)      |
| Cu(1)-Cl(2)         | 2.6922(15)    |
N(1A)-C(2A) 1.340(7)
N(1A)-C(6A) 1.341(7)
C(2A)-C(3A) 1.380(7)
C(2A)-H(2A) 0.9500
O(1W)-O(3W) 1.354(12)
C(3A)-C(4A) 1.397(8)
C(3A)-H(3A) 0.9500
C(4A)-C(5A) 1.376(8)
C(4A)-C(7A) 1.522(8)
C(5A)-C(6A) 1.385(7)
C(5A)-H(5A) 0.9500
C(6A)-H(6A) 0.9500
C(7A)-O(8A) 1.379(7)
C(7A)-O(9A) 1.407(8)
C(7A)-H(7A) 1.0000
O(8A)-C(11A) 1.415(8)
O(9A)-H(9A) 0.8400
C(11A)-H(8A1) 0.9800
C(11A)-H(8A2) 0.9800
C(11A)-H(8A3) 0.9800
N(1B)-C(2B) 1.343(7)
N(1B)-C(6B) 1.348(6)
C(2B)-C(3B) 1.374(7)
C(2B)-H(2B) 0.9500
C(3B)-C(4B) 1.392(6)
C(3B)-H(3B) 0.9500
C(4B)-C(5B) 1.386(7)
C(4B)-C(7B) 1.505(7)
C(5B)-C(6B) 1.377(7)
C(5B)-H(5B) 0.9500
C(6B)-H(6B) 0.9500
C(7B)-O(9B) 1.341(9)
C(7B)-O(10B) 1.365(8)
C(7B)-O(8B) 1.385(6)
O(8B)-C(11B) 1.419(8)
O(9B)-H(9B) 0.8400
O(10B)-H(10) 0.8400
C(11B)-H(8B1) 0.9800
C(11B)-H(8B2) 0.9800
C(11B)-H(8B3) 0.9800
N(1C)-C(2C)  1.327(6)
N(1C)-C(6C)  1.352(6)
C(2C)-C(3C)  1.375(7)
C(2C)-H(2C)  0.9500
C(3C)-C(4C)  1.388(7)
C(3C)-H(3C)  0.9500
C(4C)-C(5C)  1.393(8)
C(4C)-C(7C)  1.511(8)
C(5C)-C(6C)  1.360(7)
C(5C)-H(5C)  0.9500
C(6C)-H(6C)  0.9500
C(7C)-O(8C2)  1.325(15)
C(7C)-O(9C)  1.356(13)
C(7C)-O(10C)  1.436(18)
C(7C)-O(8C1)  1.437(10)
N(1D)-C(6D)  1.336(6)
N(1D)-C(2D)  1.336(6)
C(2D)-C(3D)  1.369(8)
C(2D)-H(2D)  0.9500
C(3D)-C(4D)  1.367(7)
C(3D)-H(3D)  0.9500
C(4D)-C(5D)  1.389(7)
C(4D)-C(7D)  1.514(7)
C(5D)-C(6D)  1.385(7)
C(5D)-H(5D)  0.9500
C(6D)-H(6D)  0.9500
C(7D)-O(8D)  1.364(6)
C(7D)-O(9D)  1.396(9)
C(7D)-O(10D)  1.397(9)
O(8D)-C(11D)  1.426(7)
O(9D)-H(9D4)  0.8400
O(10D)-H(8D5)  0.8400
C(11D)-H(8D1)  0.9800
C(11D)-H(8D2)  0.9800
C(11D)-H(8D3)  0.9800
O(9C)-H(9C1)  0.8400
O(10C)-H(10C)  0.8400
C(1C1)-O(8C1)  1.403(18)
C(1C1)-H(1CA)  0.9800
C(1C1)-H(1CB)  0.9800
C(1C1)-H(1CC) 0.9800
C(1C2)-O(8C2) 1.48(3)
C(1C2)-H(1CD) 0.9800
C(1C2)-H(1CE) 0.9800
C(1C2)-H(1CF) 0.9800
N(1B)-Cu(1)-N(1D) 176.00(16)
N(1B)-Cu(1)-N(1C) 89.92(16)
N(1D)-Cu(1)-N(1C) 89.94(16)
N(1B)-Cu(1)-N(1A) 89.84(16)
N(1D)-Cu(1)-N(1A) 90.06(16)
N(1C)-Cu(1)-N(1A) 176.56(18)
N(1B)-Cu(1)-Cl(2) 92.69(12)
N(1D)-Cu(1)-Cl(2) 91.32(12)
N(1C)-Cu(1)-Cl(2) 92.12(13)
N(1A)-Cu(1)-Cl(2) 91.32(13)
C(2A)-N(1A)-C(6A) 117.9(4)
C(2A)-N(1A)-Cu(1) 120.6(4)
C(6A)-N(1A)-Cu(1) 121.4(3)
N(1A)-C(2A)-C(3A) 122.5(5)
N(1A)-C(2A)-H(2A) 118.8
C(3A)-C(2A)-H(2A) 118.8
C(2A)-C(3A)-C(4A) 119.6(5)
C(2A)-C(3A)-H(3A) 120.2
C(4A)-C(3A)-H(3A) 120.2
C(5A)-C(4A)-C(3A) 117.6(5)
C(5A)-C(4A)-C(7A) 121.4(5)
C(3A)-C(4A)-C(7A) 120.9(5)
O(1W)#1-O(3W)-O(1W) 180.0
C(4A)-C(5A)-C(6A) 119.6(5)
C(4A)-C(5A)-H(5A) 120.2
C(6A)-C(5A)-H(5A) 120.2
N(1A)-C(6A)-C(5A) 122.8(5)
N(1A)-C(6A)-H(6A) 118.6
C(5A)-C(6A)-H(6A) 118.6
O(8A)-C(7A)-O(9A) 113.0(5)
O(8A)-C(7A)-C(4A) 106.6(4)
O(9A)-C(7A)-C(4A) 112.7(5)
O(8A)-C(7A)-H(7A) 108.1
O(9A)-C(7A)-H(7A) 108.1
C(4A)-C(7A)-H(7A) 108.1
C(7A)-O(8A)-C(11A)  112.7(5)
C(7A)-O(9A)-H(9A)  109.5
O(8A)-C(11A)-H(8A1)  109.5
O(8A)-C(11A)-H(8A2)  109.5
H(8A1)-C(11A)-H(8A2)  109.5
O(8A)-C(11A)-H(8A3)  109.5
H(8A1)-C(11A)-H(8A3)  109.5
H(8A2)-C(11A)-H(8A3)  109.5
C(2B)-N(1B)-C(6B)  117.9(4)
C(2B)-N(1B)-Cu(1)  121.2(3)
C(6B)-N(1B)-Cu(1)  120.9(3)
N(1B)-C(2B)-C(3B)  123.2(4)
N(1B)-C(2B)-H(2B)  118.4
C(3B)-C(2B)-H(2B)  118.4
C(2B)-C(3B)-C(4B)  118.7(4)
C(2B)-C(3B)-H(3B)  120.7
C(4B)-C(3B)-H(3B)  120.7
C(5B)-C(4B)-C(3B)  118.4(4)
C(5B)-C(4B)-C(7B)  122.0(4)
C(3B)-C(4B)-C(7B)  119.7(4)
C(6B)-C(5B)-C(4B)  119.6(4)
C(6B)-C(5B)-H(5B)  120.2
C(4B)-C(5B)-H(5B)  120.2
N(1B)-C(6B)-C(5B)  122.2(5)
N(1B)-C(6B)-H(6B)  118.9
C(5B)-C(6B)-H(6B)  118.9
O(9B)-C(7B)-O(10B)  98.7(5)
O(9B)-C(7B)-O(8B)  113.5(6)
O(10B)-C(7B)-O(8B)  116.8(5)
O(9B)-C(7B)-C(4B)  109.8(5)
O(10B)-C(7B)-C(4B)  111.3(5)
O(8B)-C(7B)-C(4B)  106.6(4)
C(7B)-O(8B)-C(11B)  113.3(4)
C(7B)-O(9B)-H(9B)  109.5
C(7B)-O(10B)-H(10)  109.5
O(8B)-C(11B)-H(8B1)  109.5
O(8B)-C(11B)-H(8B2)  109.5
H(8B1)-C(11B)-H(8B2)  109.5
O(8B)-C(11B)-H(8B3)  109.5
H(8B1)-C(11B)-H(8B3)  109.5
| Bond                        | Angle  |
|-----------------------------|--------|
| H(8B2)-C(11B)-H(8B3)       | 109.5  |
| C(2C)-N(1C)-C(6C)          | 117.8(4) |
| C(2C)-N(1C)-Cu(1)          | 121.4(3) |
| C(6C)-N(1C)-Cu(1)          | 120.8(3) |
| N(1C)-C(2C)-C(3C)          | 123.0(4) |
| N(1C)-C(2C)-H(2C)          | 118.5  |
| C(3C)-C(2C)-H(2C)          | 118.5  |
| C(2C)-C(3C)-C(4C)          | 119.5(5) |
| C(2C)-C(3C)-H(3C)          | 120.2  |
| C(4C)-C(3C)-H(3C)          | 120.2  |
| C(3C)-C(4C)-C(5C)          | 117.2(5) |
| C(3C)-C(4C)-C(7C)          | 120.8(5) |
| C(5C)-C(4C)-C(7C)          | 122.0(5) |
| C(6C)-C(5C)-C(4C)          | 119.9(5) |
| C(6C)-C(5C)-H(5C)          | 120.0  |
| C(4C)-C(5C)-H(5C)          | 120.0  |
| N(1C)-C(6C)-C(5C)          | 122.5(5) |
| N(1C)-C(6C)-H(6C)          | 118.7  |
| C(5C)-C(6C)-H(6C)          | 118.7  |
| O(8C2)-C(7C)-O(10C)        | 114.0(11) |
| O(9C)-C(7C)-O(8C1)         | 108.3(7) |
| O(8C2)-C(7C)-C(4C)         | 107.3(8) |
| O(9C)-C(7C)-C(4C)          | 111.1(7) |
| O(10C)-C(7C)-C(4C)         | 110.7(8) |
| O(8C1)-C(7C)-C(4C)         | 105.3(5) |
| C(6D)-N(1D)-C(2D)          | 118.2(4) |
| C(6D)-N(1D)-Cu(1)          | 120.4(3) |
| C(2D)-N(1D)-Cu(1)          | 121.4(3) |
| N(1D)-C(2D)-C(3D)          | 122.8(5) |
| N(1D)-C(2D)-H(2D)          | 118.6  |
| C(3D)-C(2D)-H(2D)          | 118.6  |
| C(4D)-C(3D)-C(2D)          | 119.6(5) |
| C(4D)-C(3D)-H(3D)          | 120.2  |
| C(2D)-C(3D)-H(3D)          | 120.2  |
| C(3D)-C(4D)-C(5D)          | 118.3(5) |
| C(3D)-C(4D)-C(7D)          | 119.5(4) |
| C(5D)-C(4D)-C(7D)          | 122.2(5) |
| C(6D)-C(5D)-C(4D)          | 119.1(5) |
| C(6D)-C(5D)-H(5D)          | 120.5  |
| C(4D)-C(5D)-H(5D)          | 120.5  |
N(1D)-C(6D)-C(5D) 122.0(4)
N(1D)-C(6D)-H(6D) 119.0
C(5D)-C(6D)-H(6D) 119.0
O(8D)-C(7D)-O(9D) 111.5(5)
O(8D)-C(7D)-O(10D) 112.7(5)
O(9D)-C(7D)-O(10D) 104.9(6)
O(8D)-C(7D)-C(4D) 107.3(4)
O(9D)-C(7D)-C(4D) 109.7(5)
O(10D)-C(7D)-C(4D) 110.7(5)
C(7D)-O(8D)-C(11D) 114.2(4)
C(7D)-O(9D)-H(9D4) 109.5
C(7D)-O(10D)-H(8D5) 109.5
O(8D)-C(11D)-H(8D1) 109.5
O(8D)-C(11D)-H(8D2) 109.5
H(8D1)-C(11D)-H(8D2) 109.5
H(8D1)-C(11D)-H(8D3) 109.5
H(8D2)-C(11D)-H(8D3) 109.5
C(7C)-O(9C)-H(9C1) 109.5
C(7C)-O(10C)-H(10C) 109.5
O(8C1)-C(1C1)-H(1CA) 109.5
O(8C1)-C(1C1)-H(1CB) 109.5
H(1CA)-C(1C1)-H(1CB) 109.5
O(8C1)-C(1C1)-H(1CC) 109.5
H(1CA)-C(1C1)-H(1CC) 109.5
H(1CB)-C(1C1)-H(1CC) 109.5
C(1C1)-O(8C1)-C(7C) 110.8(9)
O(8C2)-C(1C2)-H(1CD) 109.5
O(8C2)-C(1C2)-H(1CE) 109.5
H(1CD)-C(1C2)-H(1CE) 109.5
O(8C2)-C(1C2)-H(1CF) 109.5
H(1CD)-C(1C2)-H(1CF) 109.5
H(1CE)-C(1C2)-H(1CF) 109.5
C(7C)-O(8C2)-C(1C2) 109.9(14)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2/3,-y+4/3,-z+1/3

**Table S3.** Torsion angles [°] for 4-pyridinecarboxaldehyde with CuCl2/CH3OH (AC12_100K_2_0m)
C(6A)-N(1A)-C(2A)-C(3A)  -0.3(7)
Cu(1)-N(1A)-C(2A)-C(3A)  177.5(4)
N(1A)-C(2A)-C(3A)-C(4A)  -1.0(8)
C(2A)-C(3A)-C(4A)-C(5A)  1.2(7)
C(2A)-C(3A)-C(4A)-C(7A)  -178.8(5)
C(3A)-C(4A)-C(5A)-C(6A)  -0.2(8)
C(7A)-C(4A)-C(5A)-C(6A)  179.9(5)
C(2A)-N(1A)-C(6A)-C(5A)  1.4(8)
Cu(1)-N(1A)-C(6A)-C(5A)  -176.4(4)
C(4A)-C(5A)-C(6A)-N(1A)  -1.2(8)
C(5A)-C(4A)-C(7A)-O(8A)  -143.2(5)
C(3A)-C(4A)-C(7A)-O(8A)  36.8(7)
C(5A)-C(4A)-C(7A)-O(9A)  -18.6(7)
C(3A)-C(4A)-C(7A)-O(9A)  161.4(5)
O(9A)-C(7A)-O(8A)-C(11A)  68.5(8)
C(4A)-C(7A)-O(8A)-C(11A)  -167.1(7)
C(6B)-N(1B)-C(2B)-C(3B)  -0.6(7)
Cu(1)-N(1B)-C(2B)-C(3B)  179.3(4)
N(1B)-C(2B)-C(3B)-C(4B)  0.8(7)
C(2B)-C(3B)-C(4B)-C(5B)  0.0(7)
C(2B)-C(3B)-C(4B)-C(7B)  179.9(4)
C(3B)-C(4B)-C(5B)-C(6B)  -0.9(7)
C(7B)-C(4B)-C(5B)-C(6B)  179.2(4)
C(2B)-N(1B)-C(6B)-C(5B)  -0.4(7)
Cu(1)-N(1B)-C(6B)-C(5B)  179.6(4)
C(4B)-C(5B)-C(6B)-N(1B)  1.2(7)
C(5B)-C(4B)-C(7B)-O(9B)  121.9(6)
C(3B)-C(4B)-C(7B)-O(9B)  -58.0(7)
C(5B)-C(4B)-C(7B)-O(10B)  13.6(7)
C(3B)-C(4B)-C(7B)-O(10B)  -166.3(5)
C(5B)-C(4B)-C(7B)-O(8B)  -114.8(5)
C(3B)-C(4B)-C(7B)-O(8B)  65.3(5)
O(9B)-C(7B)-O(8B)-C(11B)  -55.9(7)
O(10B)-C(7B)-O(8B)-C(11B)  58.0(7)
C(4B)-C(7B)-O(8B)-C(11B)  -176.9(5)
C(6C)-N(1C)-C(2C)-C(3C)  -1.0(8)
Cu(1)-N(1C)-C(2C)-C(3C)  178.5(4)
N(1C)-C(2C)-C(3C)-C(4C)  -0.3(8)
C(2C)-C(3C)-C(4C)-C(5C)  0.7(8)
C(2C)-C(3C)-C(4C)-C(7C)  -179.4(5)
C(3C)-C(4C)-C(5C)-C(6C)  0.2(8)
C(7C)-C(4C)-C(5C)-C(6C)  -179.7(5)
C(2C)-N(1C)-C(6C)-C(5C)  1.9(8)
Cu(1)-N(1C)-C(6C)-C(5C)  -177.6(4)
C(4C)-C(5C)-C(6C)-N(1C)  -1.5(8)
C(3C)-C(4C)-C(7C)-O(8C2)  73.2(11)
C(5C)-C(4C)-C(7C)-O(8C2) -106.9(10)
C(3C)-C(4C)-C(7C)-O(9C)  154.0(7)
C(5C)-C(4C)-C(7C)-O(9C)  -26.1(9)
C(3C)-C(4C)-C(7C)-O(10C) 128.0(9)
C(5C)-C(4C)-C(7C)-O(8C1)  37.0(8)
C(5C)-C(4C)-C(7C)-O(8C1) -143.2(6)
C(6D)-N(1D)-C(2D)-C(3D)  0.4(7)
Cu(1)-N(1D)-C(2D)-C(3D)  -178.7(4)
N(1D)-C(2D)-C(3D)-C(4D)  0.0(8)
C(2D)-C(3D)-C(4D)-C(5D) -0.4(7)
C(2D)-C(3D)-C(4D)-C(7D)  -179.9(5)
C(3D)-C(4D)-C(5D)-C(6D)  0.4(7)
C(7D)-C(4D)-C(5D)-C(6D)  179.9(5)
C(2D)-N(1D)-C(6D)-C(5D) -0.5(8)
Cu(1)-N(1D)-C(6D)-C(5D)  178.7(4)
C(4D)-C(5D)-C(6D)-N(1D)  0.1(8)
C(3D)-C(4D)-C(7D)-O(8D) -140.8(5)
C(5D)-C(4D)-C(7D)-O(8D)  39.7(7)
C(3D)-C(4D)-C(7D)-O(9D) -19.5(7)
C(5D)-C(4D)-C(7D)-O(9D)  161.0(5)
C(3D)-C(4D)-C(7D)-O(10D) 95.8(6)
C(5D)-C(4D)-C(7D)-O(10D) -83.7(7)
O(9D)-C(7D)-O(8D)-C(11D)  57.7(7)
O(10D)-C(7D)-O(8D)-C(11D) -59.9(7)
C(4D)-C(7D)-O(8D)-C(11D)  177.9(5)
O(9C)-C(7C)-O(8C1)-C(1C1)  58.3(12)
C(4C)-C(7C)-O(8C1)-C(1C1)  177.2(9)
O(10C)-C(7C)-O(8C2)-C(1C2) -76.6(17)
C(4C)-C(7C)-O(8C2)-C(1C2)  160.4(13)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2/3,-y+4/3,z+1/3
Table S4. Hydrogen bonds for 4-pyridinecarboxaldehyde with CuCl2/CH3OH (AC12_100K_2_0m) [Å and °].

| D-H...A                  | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|-------------------------|--------|----------|----------|--------|
| C(2A)-H(2A)...Cl(3)    | 0.95   | 2.75     | 3.365(5) | 123.1  |
| C(6A)-H(6A)...Cl(2)    | 0.95   | 2.83     | 3.368(5) | 116.8  |
| C(6A)-H(6A)...O(8C2^b)#2 | 0.95   | 2.47     | 3.279(16)| 143.7  |
| C(7A)-H(7A)...Cl(2)#2 | 1.00   | 2.92     | 3.868(6) | 159.3  |
| O(9A)-H(9A)...O(9B)#3 | 0.84   | 1.70     | 2.532(9) | 169.5  |
| C(11A)-H(8A2)...Cl(3)#4 | 0.98   | 2.89     | 3.826(8) | 160.9  |
| C(2B)-H(2B)...Cl(3)    | 0.95   | 2.87     | 3.396(5) | 116.1  |
| C(6B)-H(6B)...Cl(2)    | 0.95   | 2.94     | 3.450(5) | 115.1  |
| C(6B)-H(6B)...O(8B)#4 | 0.95   | 2.56     | 3.352(6) | 140.6  |
| O(9B)-H(9B)...Cl(2)#4 | 0.84   | 2.06     | 2.887(8) | 167.8  |
| O(10B)-H(10)...Cl(2)#4 | 0.84   | 2.69     | 3.151(7) | 115.8  |
| C(11B)-H(8B2)...Cl(2)#5 | 0.98   | 2.76     | 3.700(7) | 161.8  |
| C(2C)-H(2C)...Cl(3)    | 0.95   | 2.87     | 3.470(5) | 121.9  |
| C(2C)-H(2C)...O(8D)#6 | 0.95   | 2.63     | 3.300(6) | 127.7  |
| C(6C)-H(6C)...Cl(2)    | 0.95   | 2.85     | 3.388(5) | 117.3  |
| C(2D)-H(2D)...Cl(2)    | 0.95   | 2.76     | 3.340(5) | 119.8  |
| C(6D)-H(6D)...Cl(3)    | 0.95   | 2.76     | 3.409(5) | 125.8  |
| O(9D)-H(9D4)...Cl(3)#6 | 0.84   | 2.11     | 2.873(8) | 151.6  |
| C(11D)-H(8D2)...Cl(3)#2 | 0.98   | 2.88     | 3.785(7) | 153.8  |
| O(10C^b)-H(10C^b)...O(10C^b)#7 / 0.84 | 2.38   | 3.14(3)  | 150.2  |
| C(1C2^b)-H(1CD^b)...Cl(2)#6 | 0.98   | 2.77     | 3.61(3)  | 144.5  |
| C(1C2^b)-H(1CE^b)...O(9D)#8 | 0.98   | 2.53     | 3.40(3)  | 146.6  |

Symmetry transformations used to generate equivalent atoms:

#1 -x+2/3,-y+4/3,-z+1/3  #2 x-y+1,x+1,-z  #3 -y+4/3,x-y+5/3,z-1/3
#4 y-1/3,-x+y+1/3,-z+1/3  #5 x-y+2/3,x+1/3,-z+1/3
#6 y-1,-x+y,-z  #7 -x-1/3,-y+4/3,-z+1/3  #8 -y+2/3,x-y+4/3,z+1/3
*Co(II)-4-pyridinecarboxaldehyde (CIF FILE: AC35_2_0m, CCDC 2047188)

Crystal system is trigonal, R-3, unit cell a: 24.0755(8), c: 29.5779(10) Å. 64451 reflections were collected, 6727 independents, Rint: 0.030. The structure was solved using program SHELXS-97\(^1\) and refined using the full-matrix LS procedure with SHELXL-2014/7.\(^2\) Anisotropic displacement parameters were employed for non-hydrogen atoms. All H atoms were located at the expected positions and they were refined using a riding model. H atoms for water molecule were located in the Fourier difference density map. LS weights of the form \(w = 1/\sigma^2(F_o^2) + (0.1514 P)^2 + 199.56 P\) where \(P = (F_o^2 + 2F_c^2)/3\), were employed. \(R[F^2 > 2\sigma(F^2)] = 0.1016, \ wR(F^2) = 0.2669\). Solvent molecules located in channels were refined with isotropic thermal parameters.

Figure S3. Crystal structure and numbering scheme for the cobalt complex for the 4-pyridinecarboxaldehyde with CoCl\(_2\)/CH\(_3\)OH. The displacement ellipsoids for the non-H atoms in the figure were drawn at the 50% probability level.
Figure S4. Crystal packing structure for the cobalt complex for the 4-pyridinecarboxaldehyde with CoCl₂/CH₃OH. The displacement ellipsoids for the non-H atoms in the figure were drawn at the 50% probability level.
| **Table S5.** Crystal data and structure refinement for 4-pyridinecarboxaldehyde with CoCl2/CH3OH (AC35_2_0m) |
|---------------------------------------------------------------|
| **Identification code** | **AC35_2_0m (CCDC 2047188)** |
| **Empirical formula** | C28 H36 Cl2 Co N4 O10.92 |
| **Formula weight** | 733.10 |
| **Temperature** | 100(2) K |
| **Wavelength** | 0.71073 Å |
| **Crystal system** | Trigonal |
| **Space group** | R -3 :H |
| **Unit cell dimensions** | a = 24.0755(8) Å  \( \alpha = 90^\circ \) |
| | b = 24.0755(8) Å  \( \beta = 90^\circ \) |
| | c = 29.5779(10) Å  \( \gamma = 120^\circ \) |
| **Volume** | 14847.3(11) Å³ |
| **Z** | 18 |
| **Density (calculated)** | 1.476 Mg/m³ |
| **Absorption coefficient** | 0.745 mm⁻¹ |
| **F(000)** | 6846 |
| **Crystal size** | 0.4 x 0.4 x 0.2 mm³ |
| **Theta range for data collection** | 2.066 to 26.403° |
| **Index ranges** | -30<=h<=30, -30<=k<=30, -36<=l<=36 |
| **Reflections collected** | 64451 |
| **Independent reflections** | 6727 [R(int) = 0.0300] |
| **Completeness to theta = 25.242°** | 99.3 % |
| **Refinement method** | Full-matrix least-squares on F² |
| **Data / restraints / parameters** | 6727 / 0 / 417 |
| **Goodness-of-fit on F²** | 1.052 |
| **Final R indices [I>2sigma(I)]** | R1 = 0.1016, wR2 = 0.2669 |
| **R indices (all data)** | R1 = 0.1291, wR2 = 0.3032 |
| **Extinction coefficient** | n/a |
| **Largest diff. peak and hole** | 1.115 and -1.156 e.Å⁻³ |
Table S6. Bond lengths [pm] and angles [°] for 4-pyridinecarboxaldehyde with CoCl$_2$/CH$_3$OH (AC35_2_0m).

| Bond                  | Length [pm] |
|-----------------------|-------------|
| Co(1)-N(1A)           | 2.146(4)    |
| Co(1)-N(1B)           | 2.158(4)    |
| Co(1)-N(1C)           | 2.159(4)    |
| Co(1)-N(1D)           | 2.174(4)    |
| Co(1)-Cl(2)           | 2.4500(15)  |
| Co(1)-Cl(1)           | 2.5023(14)  |
| N(1A)-C(2A)           | 1.340(6)    |
| N(1A)-C(6A)           | 1.346(6)    |
| C(2A)-C(3A)           | 1.377(8)    |
| C(2A)-H(30)           | 0.9500      |
| C(3A)-C(4A)           | 1.386(7)    |
| C(3A)-H(35)           | 0.9500      |
| C(4A)-C(5A)           | 1.388(7)    |
| C(4A)-C(7A)           | 1.505(8)    |
| C(5A)-C(6A)           | 1.375(7)    |
| C(5A)-H(5A)           | 0.9500      |
| C(6A)-H(34)           | 0.9500      |
| C(7A)-O(8A)           | 1.313(12)   |
| C(7A)-O(10A)          | 1.362(7)    |
| C(7A)-O(9A)           | 1.372(8)    |
| O(8A)-H(8A)           | 0.8400      |
| O(9A)-H(9A)           | 0.8400      |
| O(10A)-C(11A)         | 1.422(8)    |
| C(11A)-H(32)          | 0.9800      |
| C(11A)-H(33)          | 0.9800      |
| C(11A)-H(31)          | 0.9800      |
| N(1B)-C(2B)           | 1.341(7)    |
| N(1B)-C(6B)           | 1.342(7)    |
| C(2B)-C(3B)           | 1.371(8)    |
| C(2B)-H(2B)           | 0.9500      |
| C(3B)-C(4B)           | 1.371(8)    |
| C(3B)-H(21)           | 0.9500      |
| C(4B)-C(5B)           | 1.387(7)    |
| C(4B)-C(7B)           | 1.515(8)    |
| C(5B)-C(6B)           | 1.376(8)    |
| C(5B)-H(29)           | 0.9500      |
| C(6B)-H(19)           | 0.9500      |
| C(7B)-O(8B)           | 1.332(11)   |
C(7B)-O(9B)  1.344(10)
C(7B)-O(10B)  1.351(7)
O(8B)-H(8B)  0.8400
O(9B)-H(9B)  0.8400
O(10B)-C(11B)  1.406(8)
C(11B)-H(26)  0.9800
C(11B)-H(28)  0.9800
C(11B)-H(27)  0.9800
N(1C)-C(6C)  1.328(7)
N(1C)-C(2C)  1.347(7)
C(2C)-C(3C)  1.375(8)
C(2C)-H(9)  0.9500
C(3C)-C(4C)  1.388(9)
C(3C)-H(10C)  0.9500
C(4C)-C(5C)  1.390(8)
C(4C)-C(7C)  1.504(9)
C(5C)-C(6C)  1.384(8)
C(5C)-H(5C)  0.9500
C(6C)-H(6C)  0.9500
C(7C)-O(9C)  1.385(9)
C(7C)-O(8C)  1.425(9)
C(7C)-H(6)  1.0000
O(8C)-H(8C)  0.8400
O(9C)-C(11C)  1.397(11)
C(11C)-H(11A)  0.9800
C(11C)-H(11B)  0.9800
C(11C)-H(11C)  0.9800
N(1D)-C(2D)  1.328(7)
N(1D)-C(6D)  1.339(7)
C(2D)-C(3D)  1.381(8)
C(2D)-H(11)  0.9500
C(3D)-C(4D)  1.385(8)
C(3D)-H(18)  0.9500
C(4D)-C(5D)  1.399(8)
C(4D)-C(7D)  1.513(8)
C(5D)-C(6D)  1.368(8)
C(5D)-H(17)  0.9500
C(6D)-H(16)  0.9500
C(7D)-O(8D)  1.392(7)
C(7D)-O(9D)  1.407(7)
C(7D)-H(7D)  1.0000
O(8D)-H(8D)  0.8400
O(9D)-C(10D)  1.406(8)
C(10D)-H(10)  0.9800
C(10D)-H(15)  0.9800
C(10D)-H(14)  0.9800
O(2W)-O(4W)  1.364(12)
N(1A)-Co(1)-N(1B)  179.38(15)
N(1A)-Co(1)-N(1C)  90.42(16)
N(1B)-Co(1)-N(1C)  89.86(16)
N(1A)-Co(1)-N(1D)  90.36(15)
N(1B)-Co(1)-N(1D)  89.35(16)
N(1C)-Co(1)-N(1D)  178.80(15)
N(1A)-Co(1)-Cl(2)  90.90(11)
N(1B)-Co(1)-Cl(2)  89.64(12)
N(1C)-Co(1)-Cl(2)  90.71(12)
N(1D)-Co(1)-Cl(2)  90.19(12)
N(1A)-Co(1)-Cl(1)  87.81(11)
N(1B)-Co(1)-Cl(1)  91.65(12)
N(1C)-Co(1)-Cl(1)  89.43(12)
N(1D)-Co(1)-Cl(1)  89.69(12)
Cl(2)-Co(1)-Cl(1)  178.70(5)
C(2A)-N(1A)-C(6A)  117.8(4)
C(2A)-N(1A)-Co(1)  120.6(3)
C(6A)-N(1A)-Co(1)  121.6(3)
N(1A)-C(2A)-C(3A)  123.2(5)
N(1A)-C(2A)-H(30)  118.4
C(3A)-C(2A)-H(30)  118.4
C(2A)-C(3A)-C(4A)  118.9(5)
C(2A)-C(3A)-H(35)  120.5
C(4A)-C(3A)-H(35)  120.5
C(3A)-C(4A)-C(5A)  118.1(5)
C(3A)-C(4A)-C(7A)  119.1(4)
C(5A)-C(4A)-C(7A)  122.8(4)
C(6A)-C(5A)-C(4A)  119.6(4)
C(6A)-C(5A)-H(5A)  120.2
C(4A)-C(5A)-H(5A)  120.2
N(1A)-C(6A)-C(5A)  122.3(4)
N(1A)-C(6A)-H(34)  118.8
C(5A)-C(6A)-H(34)  118.8
O(8A)-C(7A)-O(10A)  110.3(7)
O(8A)-C(7A)-O(9A)  95.4(6)
O(10A)-C(7A)-O(9A)  118.6(6)
O(8A)-C(7A)-C(4A)  113.7(7)
O(9A)-C(7A)-C(4A)  107.1(4)
O(9A)-C(7A)-C(4A)  111.6(5)
C(7A)-O(8A)-H(8A)  109.5
C(7A)-O(9A)-H(9A)  109.5
C(7A)-O(10A)-C(11A)  113.8(5)
O(10A)-C(11A)-H(32)  109.5
O(10A)-C(11A)-H(33)  109.5
H(32)-C(11A)-H(33)  109.5
O(10A)-C(11A)-H(31)  109.5
H(32)-C(11A)-H(31)  109.5
H(33)-C(11A)-H(31)  109.5
C(2B)-N(1B)-C(6B)  116.6(5)
C(2B)-N(1B)-Co(1)  123.4(3)
C(6B)-N(1B)-Co(1)  120.0(3)
N(1B)-C(2B)-C(3B)  123.1(5)
N(1B)-C(2B)-H(2B)  118.4
C(3B)-C(2B)-H(2B)  118.4
C(2B)-C(3B)-C(4B)  119.8(5)
C(2B)-C(3B)-H(21)  120.1
C(4B)-C(3B)-H(21)  120.1
C(3B)-C(4B)-C(5B)  118.3(5)
C(3B)-C(4B)-C(7B)  120.9(5)
C(5B)-C(4B)-C(7B)  120.8(5)
C(6B)-C(5B)-C(4B)  118.4(5)
C(6B)-C(5B)-H(29)  120.8
C(4B)-C(5B)-H(29)  120.8
N(1B)-C(6B)-C(5B)  123.8(5)
N(1B)-C(6B)-H(19)  118.1
C(5B)-C(6B)-H(19)  118.1
O(8B)-C(7B)-O(9B)  94.3(6)
O(8B)-C(7B)-O(10B)  115.9(7)
O(9B)-C(7B)-O(10B)  116.4(6)
O(8B)-C(7B)-C(4B)  112.8(7)
O(9B)-C(7B)-C(4B)  109.2(5)
O(10B)-C(7B)-C(4B)  107.8(4)
C(7B)-O(8B)-H(8B)  109.5
| Bond                        | Angle (°) |
|-----------------------------|-----------|
| C(7B)-O(9B)-H(9B)           | 109.5     |
| C(7B)-O(10B)-C(11B)         | 114.7(5)  |
| O(10B)-C(11B)-H(26)         | 109.5     |
| O(10B)-C(11B)-H(28)         | 109.5     |
| H(26)-C(11B)-H(28)          | 109.5     |
| O(10B)-C(11B)-H(27)         | 109.5     |
| H(26)-C(11B)-H(27)          | 109.5     |
| H(28)-C(11B)-H(27)          | 109.5     |
| C(6C)-N(1C)-C(2C)           | 116.7(5)  |
| C(6C)-N(1C)-Co(1)           | 120.1(4)  |
| C(2C)-N(1C)-Co(1)           | 123.1(4)  |
| N(1C)-C(2C)-C(3C)           | 123.5(5)  |
| N(1C)-C(2C)-H(9)            | 118.2     |
| C(3C)-C(2C)-H(9)            | 118.2     |
| C(2C)-C(3C)-C(4C)           | 119.4(5)  |
| C(2C)-C(3C)-H(10C)          | 120.3     |
| C(4C)-C(3C)-H(10C)          | 120.3     |
| C(3C)-C(4C)-C(5C)           | 117.4(5)  |
| C(3C)-C(4C)-C(7C)           | 123.1(6)  |
| C(5C)-C(4C)-C(7C)           | 119.6(6)  |
| C(6C)-C(5C)-C(4C)           | 119.2(6)  |
| C(6C)-C(5C)-H(5C)           | 120.4     |
| C(4C)-C(5C)-H(5C)           | 120.4     |
| N(1C)-C(6C)-C(5C)           | 123.7(5)  |
| N(1C)-C(6C)-H(6C)           | 118.1     |
| C(5C)-C(6C)-H(6C)           | 118.1     |
| O(9C)-C(7C)-O(8C)           | 111.4(7)  |
| O(9C)-C(7C)-C(4C)           | 105.8(5)  |
| O(8C)-C(7C)-C(4C)           | 111.0(6)  |
| O(9C)-C(7C)-H(6)            | 109.5     |
| O(8C)-C(7C)-H(6)            | 109.5     |
| C(4C)-C(7C)-H(6)            | 109.5     |
| C(7C)-O(8C)-H(8C)           | 109.5     |
| C(7C)-O(9C)-C(11C)          | 112.1(7)  |
| O(9C)-C(11C)-H(11A)         | 109.5     |
| O(9C)-C(11C)-H(11B)         | 109.5     |
| H(11A)-C(11C)-H(11B)        | 109.5     |
| O(9C)-C(11C)-H(11C)         | 109.5     |
| H(11A)-C(11C)-H(11C)        | 109.5     |
| H(11B)-C(11C)-H(11C)        | 109.5     |
$C(2D) - N(1D) - C(6D) \quad 117.3(5)$

$C(2D) - N(1D) - Co(1) \quad 122.5(4)$

$C(6D) - N(1D) - Co(1) \quad 120.2(3)$

$N(1D) - C(2D) - C(3D) \quad 123.0(5)$

$N(1D) - C(2D) - H(11) \quad 118.5$

$C(3D) - C(2D) - H(11) \quad 118.5$

$C(2D) - C(3D) - C(4D) \quad 119.7(5)$

$C(2D) - C(3D) - H(18) \quad 120.2$

$C(4D) - C(3D) - H(18) \quad 120.2$

$C(3D) - C(4D) - C(5D) \quad 117.4(5)$

$C(3D) - C(4D) - C(7D) \quad 122.4(5)$

$C(5D) - C(4D) - C(7D) \quad 120.2(5)$

$C(6D) - C(5D) - C(4D) \quad 118.7(5)$

$C(6D) - C(5D) - H(17) \quad 120.6$

$C(4D) - C(5D) - H(17) \quad 120.6$

$N(1D) - C(6D) - C(5D) \quad 123.9(5)$

$N(1D) - C(6D) - H(16) \quad 118.0$

$C(5D) - C(6D) - H(16) \quad 118.0$

$O(8D) - C(7D) - O(9D) \quad 113.8(5)$

$O(8D) - C(7D) - C(4D) \quad 112.4(5)$

$O(9D) - C(7D) - C(4D) \quad 105.9(4)$

$O(8D) - C(7D) - H(7D) \quad 108.2$

$O(9D) - C(7D) - H(7D) \quad 108.2$

$C(4D) - C(7D) - H(7D) \quad 108.2$

$C(7D) - O(8D) - H(8D) \quad 109.5$

$C(10D) - O(9D) - C(7D) \quad 114.1(5)$

$O(9D) - C(10D) - H(10) \quad 109.5$

$O(9D) - C(10D) - H(15) \quad 109.5$

$H(10) - C(10D) - H(15) \quad 109.5$

$O(9D) - C(10D) - H(14) \quad 109.5$

$H(10) - C(10D) - H(14) \quad 109.5$

$H(15) - C(10D) - H(14) \quad 109.5$

$O(2W) - O(4W) - O(2W)#1 \quad 180.0$

Symmetry transformations used to generate equivalent atoms:

#1 -x+4/3,-y+2/3,-z+2/3
**Table S7.** Torsion angles [°] for 4-pyridinecarboxaldehyde with CoCl2/CH3OH (AC35_2_0m).

| Bond                              | Torsion Angle |
|-----------------------------------|---------------|
| C(6A) - N(1A) - C(2A) - C(3A)     | -0.9(8)       |
| Co(1) - N(1A) - C(2A) - C(3A)     | 180.0(4)      |
| N(1A) - C(2A) - C(3A) - C(4A)     | 0.5(8)        |
| C(2A) - C(3A) - C(4A) - C(5A)     | -1.2(7)       |
| C(2A) - C(3A) - C(4A) - C(7A)     | 179.5(5)      |
| C(3A) - C(4A) - C(5A) - C(6A)     | 2.3(7)        |
| C(7A) - C(4A) - C(5A) - C(6A)     | -178.4(5)     |
| C(2A) - N(1A) - C(6A) - C(5A)     | 2.0(7)        |
| Co(1) - N(1A) - C(6A) - C(5A)     | -178.8(4)     |
| C(4A) - C(5A) - C(6A) - N(1A)     | -2.8(7)       |
| C(3A) - C(4A) - C(7A) - O(8A)     | 62.2(8)       |
| C(5A) - C(4A) - C(7A) - O(8A)     | -117.0(8)     |
| C(3A) - C(4A) - C(7A) - O(10A)    | -59.9(6)      |
| C(5A) - C(4A) - C(7A) - O(10A)    | 120.8(5)      |
| C(3A) - C(4A) - C(7A) - O(9A)     | 168.8(5)      |
| C(5A) - C(4A) - C(7A) - O(9A)     | -10.5(7)      |
| O(8A) - C(7A) - O(10A) - C(11A)   | 49.5(8)       |
| O(9A) - C(7A) - O(10A) - C(11A)   | -58.9(7)      |
| C(4A) - C(7A) - O(10A) - C(11A)   | 173.8(5)      |
| C(6B) - N(1B) - C(2B) - C(3B)     | 0.1(8)        |
| Co(1) - N(1B) - C(2B) - C(3B)     | 178.6(4)      |
| N(1B) - C(2B) - C(3B) - C(4B)     | 0.5(8)        |
| C(2B) - C(3B) - C(4B) - C(5B)     | -0.1(8)       |
| C(2B) - C(3B) - C(4B) - C(7B)     | -179.7(5)     |
| C(3B) - C(4B) - C(5B) - C(6B)     | -0.9(8)       |
| C(7B) - C(4B) - C(5B) - C(6B)     | 178.7(5)      |
| C(2B) - N(1B) - C(6B) - C(5B)     | -1.2(8)       |
| Co(1) - N(1B) - C(6B) - C(5B)     | -179.7(4)     |
| C(4B) - C(5B) - C(6B) - N(1B)     | 1.6(9)        |
| C(3B) - C(4B) - C(7B) - O(8B)     | 9.5(8)        |
| C(5B) - C(4B) - C(7B) - O(8B)     | -170.1(6)     |
| C(3B) - C(4B) - C(7B) - O(9B)     | -93.9(7)      |
| C(5B) - C(4B) - C(7B) - O(9B)     | 86.5(7)       |
| C(3B) - C(4B) - C(7B) - O(10B)    | 138.8(5)      |
| C(5B) - C(4B) - C(7B) - O(10B)    | -40.8(7)      |
| O(8B) - C(7B) - O(10B) - C(11B)   | -49.6(9)      |
| O(9B) - C(7B) - O(10B) - C(11B)   | 60.0(9)       |
| C(4B) - C(7B) - O(10B) - C(11B)   | -177.1(6)     |
| Bond | Distance (Å) |
|------|-------------|
| C(6C)-N(1C)-C(2C)-C(3C) | 1.3(8) |
| Co(1)-N(1C)-C(2C)-C(3C) | -180.0(4) |
| N(1C)-C(2C)-C(3C)-C(4C) | -1.5(8) |
| C(2C)-C(3C)-C(4C)-C(5C) | 1.0(8) |
| C(2C)-C(3C)-C(4C)-C(7C) | -178.2(5) |
| C(3C)-C(4C)-C(5C)-C(6C) | -0.6(9) |
| C(7C)-C(4C)-C(5C)-C(6C) | 178.7(6) |
| C(2C)-N(1C)-C(6C)-C(5C) | -179.6(5) |
| C(4C)-C(5C)-C(6C)-N(1C) | 0.5(11) |
| C(3C)-C(4C)-C(7C)-O(9C) | 119.2(8) |
| C(5C)-C(4C)-C(7C)-O(9C) | -60.0(9) |
| C(3C)-C(4C)-C(7C)-O(8C) | -119.8(7) |
| C(5C)-C(4C)-C(7C)-O(8C) | 61.0(8) |
| O(8C)-C(7C)-O(9C)-C(11C) | 68.5(14) |
| C(4C)-C(7C)-O(9C)-C(11C) | -170.7(12) |
| C(6D)-N(1D)-C(2D)-C(3D) | -2.2(8) |
| Co(1)-N(1D)-C(2D)-C(3D) | 175.5(4) |
| N(1D)-C(2D)-C(3D)-C(4D) | 1.4(9) |
| C(2D)-C(3D)-C(4D)-C(5D) | 0.5(8) |
| C(2D)-C(3D)-C(4D)-C(7D) | -178.8(5) |
| C(3D)-C(4D)-C(5D)-C(6D) | -1.4(7) |
| C(7D)-C(4D)-C(5D)-C(6D) | 177.8(5) |
| C(2D)-N(1D)-C(6D)-C(5D) | 1.1(8) |
| Co(1)-N(1D)-C(6D)-C(5D) | -176.6(4) |
| C(4D)-C(5D)-C(6D)-N(1D) | 0.7(8) |
| C(3D)-C(4D)-C(7D)-O(8D) | 16.8(7) |
| C(5D)-C(4D)-C(7D)-O(8D) | -162.4(5) |
| C(3D)-C(4D)-C(7D)-O(9D) | 141.7(5) |
| C(5D)-C(4D)-C(7D)-O(9D) | -37.5(7) |
| O(8D)-C(7D)-O(9D)-C(10D) | -66.3(8) |
| C(4D)-C(7D)-O(9D)-C(10D) | 169.6(6) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+4/3,-y+2/3,-z+2/3
Table S8. Hydrogen bonds for 4-pyridinecarboxaldehyde with CoCl$_2$/CH$_3$OH (AC35_2_0m). [pm and °].

| D-H...A                        | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|--------------------------------|--------|----------|----------|--------|
| C(6A)-H(34)...Cl(2)           | 0.95   | 2.97     | 3.415(5) | 110.4  |
| C(6A)-H(34)...O(10A)#2        | 0.95   | 2.59     | 3.417(6) | 145.7  |
| O(8A)-H(8A)...Cl(2)#2         | 0.84   | 2.13     | 2.912(13)| 155.1  |
| O(9A)-H(9A)...O(1W)           | 0.84   | 2.03     | 2.777(7) | 147.7  |
| C(11A)-H(33)...Cl(2)#3        | 0.98   | 2.89     | 3.789(8) | 152.5  |
| C(2B)-H(2B)...Cl(2)           | 0.95   | 2.80     | 3.315(6) | 115.2  |
| C(6B)-H(19)...Cl(1)           | 0.95   | 2.80     | 3.358(6) | 118.6  |
| C(11B)-H(28)...Cl(1)#4        | 0.98   | 2.99     | 3.830(9) | 144.8  |
| C(2C)-H(9)...Cl(2)            | 0.95   | 2.89     | 3.385(6) | 113.7  |
| C(6C)-H(6C)...Cl(1)           | 0.95   | 2.81     | 3.324(6) | 114.8  |
| C(6C)-H(6C)...O(10B)#5        | 0.95   | 2.56     | 3.261(7) | 130.8  |
| O(8C)-H(8C)...O(8B)#6         | 0.84   | 1.73     | 2.552(10)| 165.5  |
| C(11C)-H(11B)...Cl(2)#5       | 0.98   | 2.83     | 3.730(11)| 152.9  |
| C(2D)-H(11)...Cl(2)           | 0.95   | 2.89     | 3.356(6) | 111.8  |
| C(6D)-H(16)...Cl(1)           | 0.95   | 2.77     | 3.328(5) | 118.1  |
| O(8D)-H(8D)...O(8A)#7         | 0.84   | 1.71     | 2.528(11)| 164.7  |

Symmetry transformations used to generate equivalent atoms:

#1  -x+4/3,-y+2/3,-z+2/3  #2  y-1/3,-x+y+1/3,-z+1/3
#3  x-y+2/3,x+1/3,-z+1/3  #4  x-y+1/3,x-1/3,-z+2/3
#5  y+1/3,-x+y+2/3,-z+2/3  #6  -y+4/3,x-y+2/3,z-1/3
#7  -y+2/3,x-y+1/3,z+1/3
*Co(II)-3-pyridinecarboxaldehyde (CIF FILE: C5_0m, CCDC 2047189)

Crystal system is monoclinic, P2₁/c, unit cell: a: 7.7191(15), b: 36.122(7), c: 8.4932(17) Å, β: 92.41°. 18330 reflections were collected, 4016 independents, Rint: 0.15. The structure was solved using program SHELXS-97¹ and refined using the full-matrix LS procedure with SHELXL-2014/7.² Anisotropic displacement parameters were employed for non-hydrogen atoms. All H atoms were located at the expected positions and they were refined using a riding model. H atoms for water molecule were located in the Fourier difference density map. LS weights of the form \( w = \frac{1}{[\sigma^2(F_o^2) + (0.0313P)^2 + 6.1654P]} \) where \( P = (F_o^2 + 2F_c^2)/3 \), were employed. \( R[F^2 > 2\sigma(F^2)] = 0.065 \), \( wR(F^2) = 0.115 \).

Figure S5. Crystal structure and numbering scheme for the cobalt complex for the 3-pyridinecarboxaldehyde with CoCl₂/CH₃OH. The displacement ellipsoids for the non-H atoms in the figure were drawn at the 50% probability level.
Figure S6. Crystal packing structure for the cobalt complex for the 3-pyridinecarboxaldehyde with CoCl$_2$/CH$_3$OH. The displacement ellipsoids for the non-H atoms in the figure were drawn at the 50% probability level.
Table S9. Crystal data and structure refinement for 3-pyridinecarboxaldehyde with CoCl2/CH3OH (C5_0m)

| Property                                         | Value                                    |
|--------------------------------------------------|------------------------------------------|
| Identification code                              | C5_0m (CCDC 2047189)                    |
| Empirical formula                                | C24 H20 Cl2 Co N4 O4                    |
| Formula weight                                    | 558.27                                   |
| Temperature                                       | 293(2) K                                 |
| Wavelength                                        | 0.71073 Å                                |
| Crystal system                                    | Monoclinic                               |
| Space group                                       | P 21/c                                   |
| Unit cell dimensions                              | a = 7.7191(15) Å                        |
|                                                  | b = 36.122(7) Å                         |
|                                                  | c = 8.4932(17) Å                        |
|                                                  | α = 90°                                  |
|                                                  | β = 92.41(3)°                            |
|                                                  | γ = 90°                                  |
| Volume                                           | 2366.0(8) Å                             |
| Z                                                | 4                                        |
| Density (calculated)                             | 1.567 Mg/m³                              |
| Absorption coefficient                           | 0.991 mm⁻¹                               |
| F(000)                                           | 1140                                     |
| Crystal size                                     | 0.25 x 0.2 x 0.15 mm³                   |
| Theta range for data collection                  | 2.466 to 24.724°                         |
| Index ranges                                     | -9<=h<=9, -42<=k<=42, -9<=l<=9           |
| Reflections collected                            | 18330                                    |
| Independent reflections                          | 4016 [R(int) = 0.1501]                   |
| Completeness to theta = 24.724°                  | 99.8 %                                   |
| Absorption correction                            | Semi-empirical from equivalents         |
| Refinement method                                | Full-matrix least-squares on F²         |
| Data / restraints / parameters                    | 4016 / 0 / 316                           |
| Goodness-of-fit on F²                             | 1.106                                    |
| Final R indices [I>2sigma(I)]                    | R1 = 0.0650, wR2 = 0.1151               |
| R indices (all data)                             | R1 = 0.1276, wR2 = 0.1303               |
| Extinction coefficient                           | n/a                                      |
| Largest diff. peak and hole                      | 0.427 and -0.650 e.Å⁻³                  |
Table S10. Bond lengths [Å] and angles [°] for 3-pyridinecarboxaldehyde with CoCl2/CH3OH (C5_0m)

| Bond                  | Length/Angle |
|-----------------------|--------------|
| Co(1)-N(1A)           | 2.213(5)     |
| Co(1)-N(1D)           | 2.222(5)     |
| Co(1)-N(1B)           | 2.234(5)     |
| Co(1)-N(1C)           | 2.245(5)     |
| Co(1)-Cl(3)           | 2.4077(18)   |
| Co(1)-Cl(2)           | 2.4185(19)   |
| O(1A)-C(7A)           | 1.205(7)     |
| N(1A)-C(6A)           | 1.331(7)     |
| N(1A)-C(2A)           | 1.357(7)     |
| C(2A)-C(3A)           | 1.372(8)     |
| C(3A)-C(4A)           | 1.387(8)     |
| C(3A)-C(7A)           | 1.504(9)     |
| C(4A)-C(5A)           | 1.374(8)     |
| C(5A)-C(6A)           | 1.380(8)     |
| O(1B)-C(7B)           | 1.202(7)     |
| N(1B)-C(6B)           | 1.341(8)     |
| N(1B)-C(2B)           | 1.341(7)     |
| C(2B)-C(3B)           | 1.384(8)     |
| C(3B)-C(4B)           | 1.387(9)     |
| C(3B)-C(7B)           | 1.487(8)     |
| C(4B)-C(5B)           | 1.367(9)     |
| C(5B)-C(6B)           | 1.385(9)     |
| O(1C)-C(7C)           | 1.202(8)     |
| N(1C)-C(6C)           | 1.349(8)     |
| N(1C)-C(2C)           | 1.350(7)     |
| C(2C)-C(3C)           | 1.380(8)     |
| C(3C)-C(4C)           | 1.387(9)     |
| C(3C)-C(7C)           | 1.478(9)     |
| C(4C)-C(5C)           | 1.387(9)     |
| C(5C)-C(6C)           | 1.373(9)     |
| O(1D)-C(7D)           | 1.201(8)     |
| N(1D)-C(6D)           | 1.329(8)     |
| N(1D)-C(2D)           | 1.355(7)     |
| C(2D)-C(3D)           | 1.387(8)     |
| C(3D)-C(4D)           | 1.369(9)     |
| C(3D)-C(7D)           | 1.489(9)     |
| C(4D)-C(5D)           | 1.386(9)     |
| C(5D)-C(6D)           | 1.394(9)     |
N(1A)-Co(1)-N(1D)  89.07(18)
N(1A)-Co(1)-N(1B)  88.72(18)
N(1D)-Co(1)-N(1B)  177.8(2)
N(1A)-Co(1)-N(1C)  178.23(19)
N(1D)-Co(1)-N(1C)  89.28(18)
N(1B)-Co(1)-N(1C)  92.92(18)
N(1A)-Co(1)-Cl(3)  91.40(13)
N(1D)-Co(1)-Cl(3)  92.12(14)
N(1B)-Co(1)-Cl(3)  88.24(14)
N(1C)-Co(1)-Cl(3)  89.32(14)
N(1A)-Co(1)-Cl(2)  89.81(13)
N(1D)-Co(1)-Cl(2)  90.53(14)
N(1B)-Co(1)-Cl(2)  89.16(14)
N(1C)-Co(1)-Cl(2)  89.54(14)
Cl(3)-Co(1)-Cl(2)  177.11(7)
C(6A)-N(1A)-C(2A)  116.1(5)
C(6A)-N(1A)-Co(1)  121.3(4)
C(2A)-N(1A)-Co(1)  122.5(4)
N(1A)-C(2A)-C(3A)  122.7(6)
C(2A)-C(3A)-C(4A)  120.1(6)
C(2A)-C(3A)-C(7A)  117.8(6)
C(4A)-C(3A)-C(7A)  122.2(6)
C(5A)-C(4A)-C(3A)  117.7(6)
C(4A)-C(5A)-C(6A)  118.8(6)
N(1A)-C(6A)-C(5A)  124.6(6)
O(1A)-C(7A)-C(3A)  123.8(6)
C(6B)-N(1B)-C(2B)  116.9(6)
C(6B)-N(1B)-Co(1)  119.8(4)
C(2B)-N(1B)-Co(1)  123.2(4)
N(1B)-C(2B)-C(3B)  123.3(6)
C(2B)-C(3B)-C(4B)  118.6(6)
C(2B)-C(3B)-C(7B)  118.6(6)
C(4B)-C(3B)-C(7B)  122.7(6)
C(5B)-C(4B)-C(3B)  118.7(6)
C(4B)-C(5B)-C(6B)  119.2(6)
N(1B)-C(6B)-C(5B)  123.3(6)
O(1B)-C(7B)-C(3B)  124.2(6)
C(6C)-N(1C)-C(2C)  115.7(5)
C(6C)-N(1C)-Co(1)  120.7(4)
Table S11. Torsion angles [°] for 3-pyridinecarboxaldehyde with CoCl2/CH3OH (C5_0m)

Table 3. Torsion angles [°] for c5_0m.

| Bond | Torsion Angle |
|------|--------------|
| C(6A)-N(1A)-C(2A)-C(3A) | -0.3(9) |
| Co(1)-N(1A)-C(2A)-C(3A) | -176.9(5) |
| N(1A)-C(2A)-C(3A)-C(4A) | 2.0(10) |
| N(1A)-C(2A)-C(3A)-C(7A) | -177.9(6) |
| C(2A)-C(3A)-C(4A)-C(5A) | -2.5(9) |
| C(7A)-C(3A)-C(4A)-C(5A) | 177.3(6) |
| C(3A)-C(4A)-C(5A)-C(6A) | 1.5(9) |
| C(2A)-N(1A)-C(6A)-C(5A) | -0.8(9) |
| Co(1)-N(1A)-C(6A)-C(5A) | 175.9(5) |
| C(4A)-C(5A)-C(6A)-N(1A) | 0.2(10) |
| C(2A)-C(3A)-C(7A)-O(1A) | 176.3(6) |
| C(4A)-C(3A)-C(7A)-O(1A) | -3.5(10) |
Table S12. Hydrogen bonds for 3-pyridinecarboxaldehyde with CoCl2/CH3OH (C5_0m) [Å and °].

| D-H...A                   | d(D-H) | d(H...A) | d(D...A)   | <(DHA) |
|---------------------------|--------|----------|------------|--------|
| C(2A)-H(2A)...Cl(2)      | 0.93   | 2.75     | 3.316(6)   | 119.7  |
| C(6A)-H(6A)...Cl(3)      | 0.93   | 2.71     | 3.297(6)   | 122.0  |
| C(7A)-H(7A)...Cl(3)#1    | 0.93   | 2.77     | 3.677(7)   | 165.9  |
| C(2B)-H(2B)...Cl(3)      | 0.93   | 2.76     | 3.288(7)   | 117.3  |
| C(6B)-H(6B)...Cl(2)      | 0.93   | 2.73     | 3.277(6)   | 118.7  |
| C(7B)-H(7B)...Cl(2)#2    | 0.93   | 2.73     | 3.621(7)   | 159.9  |
| C(2C)-H(2C)...Cl(3)      | 0.93   | 2.72     | 3.325(7)   | 123.2  |
| C(6C)-H(6C)...Cl(2)      | 0.93   | 2.68     | 3.240(7)   | 119.1  |
| C(7C)-H(7C)...Cl(2)#2    | 0.93   | 2.93     | 3.830(7)   | 163.5  |
| C(2D)-H(2D)...Cl(2)      | 0.93   | 2.57     | 3.239(7)   | 128.8  |
| C(6D)-H(6D)...Cl(3)      | 0.93   | 2.61     | 3.277(7)   | 129.5  |
| C(7D)-H(7D)...Cl(3)#1    | 0.93   | 2.86     | 3.577(7)   | 134.8  |

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z      #2 x-1,y,z
Solution-state NMR studies:

Solution-state NMR experiments were performed in order to understand the complex chemical functionalization observed in the X-ray structure of these systems. NMR spectra for 4-, 3- and 2-pyridinecarboxaldehyde were acquired in CD$_3$OD to match the solvent used during complex preparation. In each case, the presence of gem-diol ($\delta(^1H) = 5.50-5.70$ ppm) and aldehyde forms ($\delta(^1H) = 10.00-10.20$ ppm) was observed. Integration of the signals provided their relative proportions. In a previous work, we reported that the addition of water molecules to the aldehyde group in pyridinecarboxaldehyde isomers is determined by the position of the group in the aromatic ring. The most reactive compound for the addition of water is the 4-pyridinecarboxaldehyde, followed by 2- and 3-pyridinecarboxaldehyde, with the fraction of gem-diol forms being 50, 40 and 10%, respectively, as determined by $^1$H solution-state NMR in D$_2$O. This phenomenon is due to the π-deficient character of the pyridine ring, with positions 2, 4 and 6 being the most electron-deficient, which explains the low degree of hydration of 3-pyridinecarboxaldehyde. Interestingly, the gem-diol content reached 95% for 4-pyridinecarboxaldehyde in CD$_3$OD. However, the NMR spectrum in CDCl$_3$ only showed the aldehyde form (Figure S8), indicating that the residual water molecules present in the deuterated methanol (water content ≤ 250 ppm) were added to the aldehyde group with higher reactivity than in D$_2$O. Corresponding results were observed for the 3-pyridinecarboxaldehyde, where the gem-diol content was 75%.
A) 4-pyridinecarboxaldehyde:

*4-pyridinecarboxaldehyde in CDCl₃: aldehyde (100%)

Figure S7. NMR spectra for the 4-pyridinecarboxaldehyde in CDCl₃. Aldehyde form (100%): ¹H NMR (600 MHz, CD₃Cl) δ (ppm) 10.06 (s, 1H, -CHO), 8.86 (d, J = 6.0 Hz, 2H, H₂,₆), 7.68 (m, 2H, H₃,₅). ¹³C NMR (151 MHz, CD₃Cl) δ (ppm) 191.55 (-CHO), 151.30 (C₂,₆), 141.52 (C₄, CHO), 122.22 (C₃,₅).
4-pyridinecarboxaldehyde in CD$_3$OD: aldehyde (4.70%), gem-diol (95.30%)

Figure S8. NMR spectra for the 4-pyridinecarboxaldehyde in CD$_3$OD. $^1$H NMR (600 MHz, CD$_3$OD) Aldehyde form (4.70%): δ (ppm) 10.08 (s, 1H, (-CHO)), 8.82 (d, J = 6.0 Hz, 2H, H$_2$), 7.84 (d, J = 6.0 Hz, 2H, H$_3$), gem-diol form (95.30%): 8.52 (d, J = 6.2 Hz, 2H, H$_2$), 7.52 (d, J = 6.1 Hz, 2H, H$_3$), 5.54 (s, 1H, (-CH(OH)$_2$)). $^{13}$C NMR (151 MHz, CD$_3$OD) Aldehyde form
(4.70%) \( \delta \) (ppm) 193.15 (-CHO), 151.79 (C\(_{2,6}\)), 143.77 (C\(_4\)), 123.64 (C\(_{3,5}\)), gem-diol form (95.30%) \( \delta \) 152.44 (C\(_4\)), 150.00 (C\(_{2,6}\)), 122.85 (C\(_{3,5}\)), 97.00 (-CH(OH)\(_2\)).

*Solution-state NMR experiments with 4-pyridinecarboxaldehyde and CuCl\(_2\)/CD\(_3\)OD:

Addition of copper ions to the deuterated methanolic solution of both 4- and 3-pyridinecarboxaldehyde produced a broadening of the NMR signals due to the relaxation effect of paramagnetic copper ions (Figure S9). In particular, the resonance of the gem-diol (RCH(OH)\(_2\)) \( \delta^1\text{H}: 5.54 \text{ and } 5.61 \text{ ppm for the 4- and 3-pyridinecarboxaldehyde, respectively} \), shifted to low-frequency values as the copper concentration increased. These peaks then fuse with that of water to produce a peak at 4.88 ppm. However, the chemical shift of the aldehyde proton (RCHO) remained unchanged, even at the highest copper concentration \( \delta^1\text{H}: 10.08 \text{ and } 10.11 \text{ ppm for the 4- and 3-pyridinecarboxaldehyde, respectively} \). The chemical shifts of the pyridine ring protons were highly affected by the addition of copper ions at any concentration and in both systems. Moreover, \(^{13}\text{C} \) NMR spectra showed that the chemical shifts of pyridine carbon atoms were highly affected and that the peaks totally disappeared at high copper concentrations (Figure S10). The same spectral changes were observed for cobalt complexes (Figures S21 and S22).

![Figure S9](image)

Figure S9. \(^1\text{H} \) solution-state NMR for 4-pyridinecarboxaldehyde (0.28 mmol) in CD\(_3\)OD and different CuCl\(_2\) additions: 0 (A), 1.21 (B), 4.86 (C), 7.29 (D) and 9.72 \( \mu \)moles (E).
Figure S10. $^{13}$C solution-state NMR spectra for 4-pyridinecarboxaldehyde (0.28 mmol) in CD$_3$OD and different CuCl$_2$ additions: 0 (A), 1.21 (B), 4.86 (C), 7.29 (D) and 9.72 $\mu$mol (E).

*Solution-state NMR experiments for the solid complex obtained for the 4-pyridindecarboxaldehyde and CuCl$_2$/CH$_3$OH dissolved in different solvents:

Figure S11. $^1$H-NMR spectrum in D$_2$O.
Figure S12. $^{13}$C-NMR spectrum in D$_2$O.

Figure S13. $^1$H-NMR spectrum in DMSO-$d_6$. 
Figure S14. $^{13}$C-NMR spectrum in DMSO-$d_6$.

Figure S15. $^1$H-NMR spectrum in CD$_3$OD.
**Figure S16.** $^{13}$C-NMR spectrum in CD$_3$OD.

**Figure S17.** $^1$H-NMR spectrum in CD$_3$CN.
Figure S18. $^{13}$C-NMR spectrum in CD$_3$CN.
B) 3-pyridinecarboxaldehyde:

*3-pyridinecarboxaldehyde in CDCl₃: aldehyde (100%)

Figure S19. NMR spectra for the 3-pyridinecarboxaldehyde in CDCl₃. Aldehyde form (100%): ¹H NMR (600 MHz, CDCl₃) δ (ppm) 10.10 (s, 1H, -CHO), 9.06 (d, J = 1.5 Hz, H₂), 8.82 (dd, J = 4.8, 1.7 Hz, H₆), 8.15 (d, J = 7.9 Hz, H₄), 7.47 (dd, J = 7.8, 4.8 Hz, H₅). ¹³C NMR (151 MHz, CDCl₃) δ (ppm) 190.74 (-CHO), 154.69 (C₆), 152.17 (C₂), 135.80 (C₄), 131.49 (C₃), 124.07 (C₅).
*3-pyridinecarboxaldehyde in CD$_3$OD: aldehyde (25%), gem-diol (75%)

Figure S20. NMR spectra for the 3-pyridinecarboxaldehyde in CD$_3$OD. $^1$H NMR (600 MHz, CD$_3$OD) Aldehyde form (25.0%): $\delta$ (ppm) 10.11 (s, 1H, (-CHO)), 9.05 (s, 1H, Hz), 8.79 (d, $J$ = 3.6 Hz, 1H, H$_6$), 8.30 (d, $J$ = 7.9 Hz, 1H, H$_4$), 7.63 (dd, $J$ = 7.9 Hz, $J$ = 5.0 Hz, 1H, H$_5$). gem-diol
form (75.0%): 8.63 (s, 1H, H2), 8.48 (d, J = 4.9 Hz, 1H, H6), 7.93 (d, J = 7.9 Hz, 1H, H4), 7.43 (dd, J = 7.9 Hz, J = 4.9 Hz, 1H, H5), 5.61 (s, 1H, -CH(OH)2). 13C NMR (151 MHz, CD3OD) Aldehyde form (25.0%): δ (ppm) 191.20 (-CHO), 153.71 (C6), 150.75 (C2), 137.76 (C3), 132.06 (C4), 124.44 (C5) gem-diol form (75.0%): 148.20 (C6), 146.89 (C2), 136.50 (C3), 134.79 (C4) 123.50 (C5), 95.32 (-CH(OH)2).

*Solution-state NMR experiments with 3-pyridinedecarboxaldehyde and CoCl2/CD3OD:

Figure S21. 1H solution-state NMR for 3-pyridinedecarboxaldehyde (0.28 mmol) in CD3OD and different CoCl2 additions: 0 (A), 1.83 (B), 5.49 (C), 7.32 (D) and 9.0 μmoles (E).
Figure S22. $^{13}$C solution-state NMR spectra for 3-pyridinecarboxaldehyde (0.28 mmol) in CD$_3$OD and different CoCl$_2$ additions: 0 (A), 1.83 (B), 5.49 (C), 7.32 (D) and 9.0 $\mu$moles (E).

*Solution-state NMR experiments with 3-pyridindecarboxaldehyde and CuCl$_2$/CD$_3$OD:

Figure S23. $^1$H-NMR spectrum in CD$_3$OD.
Figure S24. $^{13}$C-NMR spectrum in CD$_3$OD.
Coordinates x,y,z for the DFT calculations:

*Cu(II)-4-piridinecarboxaldehyde

Cu, 0,-0.0132942578,-0.10134342,0.0455736234
C, 0.2686933239,0.5743059052,1.1280228658
C, 0.27857349022,-0.5623989964,-0.8795918029
C, 0.4689518609,0.6366230684,1.2072072674
H, 0.20397191946,0.967618745,1.9063790086
C, 0.41746611699,-0.5514871418,-0.865976889
H, 0.215888519,-0.9824284486,-1.7034532151
H, 0.4547559302,1.1294752302,0.0457441735
H, 0.47325561626,-0.9960117766,-1.6812409605
C, 0,-0.3745888812,-2.8931693693,-0.9678324406
C, 0.6034547521,-2.8168920081,1.124256941
C, -0.3324362168,-4.2799372119,-0.9828453073
H, -0.7430584452,-3.2117174865,-1.8085137083
C, 0.6901332573,-4.2005933114,1.1763266733
H, 0.9231993019,-1.7946837383,1.9409056804
H, -0.6999387947,-4.8286003281,-1.8425545859
H, 0.1132064148,-4.6865959173,0.0382512904
C, -2.7615778967,0.298632749,-1.0665194781
C, -2.7750623137,-0.7403251248,0.9954951288
C, -4.1450343258,0.2552353234,-1.1416918704
H, -2.1441883675,0.6945629868,-1.8679045847
C, -4.1611687601,-0.8317385907,0.9884280896
H, -2.1732837142,-1.0788014348,1.8343770691
H, -4.6585541156,0.6566626119,-2.0085645283
H, -4.6857384486,-1.2837216181,1.8185488359
C, 0.4731641173,2.6588048101,-0.9714978583
C, -0.7398909387,2.6330468184,0.9929528828
C, 0.4287509674,4.0451982409,-1.0295934236
H, 0.9464632523,2.059991202,-1.7437877209
C, -0.840543425,0.157744289,0.9975666189
H, -1.141505534,0.0167381102,1.7918353432
H, 0.9230160001,4.5732395916,-1.8371502926
H, -1.3600282828,4.5255937148,1.8005138308
C, 0.48325540695,0.058847291,0.1962994803
C, -0.4828748123,-0.3251274769,-0.0991925178
C, -0.2461957631,4.74080982,-0.0307985211
C, 0.211273165,-4.9531043123,0.108102656
N, 0,-1.012669859,1.9683256067,0.0203226164
N, -0.20906598426,-0.19050970,-0.0144172254
N, 0.0796043471,-2.1762043299,0.0684777874
N, 0.2058776016,-0.0170579786,0.1018973036
C, 0.2319958767,-6.4605014385,0.1608192862
H, -0.7116104466,-6.8181891827,0.6188545622
O, 0.13118808261,-6.8703477458,0.9517537892
H, 0.1104616056,-7.7332769036,1.3312028118
O, 0.2945836873,-6.9341493337,-1.1506785027
C, 0.1769887996,-8.3304928624,-1.245849073
H, 0.01196249564,-8.5750181217,-2.3082279621
*Complex Cu(II)-3-pyridinecarboxaldehyde*
Magnetic shielding constant $\sigma_{\text{orb}}$ for the standard TMS (in ppm)

| Nuclei | Value (PBE0-D3, 6-31G**(d,p)) |
|--------|-------------------------------|
| $^{13}\text{C}$ | 185 |
Table S13. g/A tensors obtained by computational calculations. The experimental g/A-values are included for comparison.

|                  | Experimental | Computational Calculations |                  |
|------------------|--------------|----------------------------|------------------|
|                  | g/A          | g/A (MHz)                  | g/A eigenvectors |
| Cu(II)-4-        | 2.246 / n.d. | 2.255 / 565.7              | [0.0067683, 0.0246772, 0.9996726] |
| pyridinecarboxaldehyde |              |                            | [0.0238158, -0.0059625, 0.9996986] |
|                  | 2.067 / n.d. | 2.082 / 51.1               | [-0.9952482, -0.0972379, 0.0043371] |
|                  |              |                            | [-0.9963194, -0.0822241, 0.0242257] |
|                  | 2.030 / n.d. | 2.079 / 57.4               | [0.0971350, -0.9949517, -0.0252183] |
|                  |              |                            | [0.0823437, -0.9965960, -0.0039823] |
| Cu(II)-3-        | 2.215 / 117  | 2.237 / 578.3              | [0.0000099, -0.3457802, 0.9383156] |
| pyridinecarboxaldehyde |              |                            | [0.3454985, -0.0000016, 0.9384193] |
|                  | 2.084 / n.d. | 2.073 / 15.3               | [-1.0000000, 0.0001710, 0.0000735] |
|                  |              |                            | [-0.9384193, -0.0002015, 0.3454985] |
|                  | 2.055 / 161  | 2.068 / 33.1               | [-0.0001858, -0.9383155, -0.3457801] |
|                  |              |                            | [0.0001885, -1.0000000, -0.0000711] |

n.d., non-detectable.
A-values in MHz

Atom coordinates of the copper(II) centers of Cu(II)-4- pyridinecarboxaldehyde complex:
Cu  -0.01254000 -0.09639600 0.06301300
N   -0.19266900 1.96738300 0.04643400
N   -2.08408100 -0.27776400 0.00991000
N   -0.17273600 -2.16519000 0.07720700
N   -2.05371700 0.07986600 0.11244900
Cl  -0.08176200 -0.07483100 2.74177300
Cl  -0.05374500 -0.09935700 -2.62653700

Atom coordinates of the copper(II) centers of Cu(II)-3-pyridinecarboxaldehyde complex:
Cu  -0.22514800 -0.00005500 -0.73600600
N   -0.12783400 -2.03542900 -0.46932900
N   -2.04311900 -0.00036400 0.23918200
N   -1.78920500 0.00029900 -1.16168800
N   -0.12855600 2.03535400 -0.46932700
Cl  -1.06553100 -0.00008000 3.03286000
Cl  -1.06875500 0.00008300 2.80074800

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Figure S25. g/A-tensor orientations of the copper(II) centers of Cu(II)-4-pyridinecarboxaldehyde (A) and Cu(II)-3-pyridinecarboxaldehyde (B) in the molecular frame A-eigenvectors in panel A are omitted for clarity, but as shown in table S13, they are nearly coincidental to those of g-eigenvectors.
Table S14. EPR parameters and its contribution to pNMR shielding tensor for the Cu(II)-4-pyridinecarboxaldehyde (Complex 1) and Cu(II)-3-pyridinecarboxaldehyde (Complex 2) (g is dimensionless, and A is in MHz).

| Nucleus | Property | Complex 1 (Orthoester) | Complex 1 (Hemiacetal) | Complex 2 |
|---------|----------|------------------------|------------------------|-----------|
|         | g_{iso}  | 2.1387221              | 2.1258158              |           |
| C_{2}   | \sigma_{iso(orb)} | 27.6                  | 28.2                  | 22.5      |
|         | A_{iso}  | -0.8413                | -0.7058                | -0.1142   |
|         | g_{e-AFC} | -1.685                 | -1.413                 | -0.2286   |
|         | \Delta g_{iso-A_{FC}} | -0.1148              | -0.09627               | -0.01409  |
|         | \Delta g_{aniso-A_{dip}} | 0.0                  | 0.0                   | 0.0       |
| C_{3}   | \sigma_{iso(orb)} | 64.3                  | 64.3                  | 50.9      |
|         | A_{iso}  | 3.488                  | 3.474                  | 3.573     |
|         | g_{e-AFC} | 6.983                 | 6.957                  | 7.155     |
|         | \Delta g_{iso-A_{FC}} | 0.4757               | 0.4740                 | 0.4413    |
|         | \Delta g_{aniso-A_{dip}} | 0                    | 0                     | 0         |
| C_{4}   | \sigma_{iso(orb)} | 31.5                  | 33.0                  | 46.0      |
|         | A_{iso}  | -0.8651                | -0.8644                | -0.9075   |
|         | g_{e-AFC} | -1.732                | -1.731                 | -1.817    |
|         | \Delta g_{iso-A_{FC}} | -0.1180              | -0.1179                | -0.1121   |
|         | \Delta g_{aniso-A_{dip}} | 0                    | 0                     | 0         |
| C_{5}   | \sigma_{iso(orb)} | 64.8                  | 64.5                  | 59.8      |
|         | A_{iso}  | 3.449                  | 3.461                  | 3.704     |
|         | g_{e-AFC} | 6.907                 | 6.930                  | 7.416     |
|         | \Delta g_{iso-A_{FC}} | 0.4705               | 0.4721                 | 0.4574    |
|         | \Delta g_{aniso-A_{dip}} | 0                    | 0                     | 0         |
| C_{6}   | \sigma_{iso(orb)} | 27.6                  | 27.8                  | 25.6      |
|         | $A_{iso}$ | $g_{e, AFC}$ | $\Delta g_{iso, AFC}$ | $\Delta g_{aniso, A_{dip}}$ |
|---------|-----------|--------------|------------------------|-----------------------------|
| CH(OH)(OCH$_3$) (C$_7$) | -0.8506   | -1.703       | -0.1160                | 0                           |
|         | -0.8094   | -1.621       | -0.1104                | 0                           |
|         | -1.258    | -2.519       | -0.1553                | 0                           |
|         | $\sigma_{iso}$ | 90.6         | 0                      | 0                           |
| -C(OH)$_2$(OCH$_3$) (C$_7$) | 0.2248     | 0.4501       | 0.03066                | 0                           |
|         | 0.007609  | 0.006608     | 0.0005183              | 0                           |
|         | 0.0038    | 0.0033       | 0.0004501              | 0                           |
|         | 0.03307   | 0.03066      | 0.0005183              | 0                           |
|         | 0         | 0            | 0                      | 0                           |
| -OCH$_3$ (C$_8$) | 0.0038    | 0.0033       | 0.0005183              | 0                           |
|         | 0.007609  | 0.006608     | 0.0005183              | 0                           |
|         | 0.0038    | 0.0033       | 0.0004501              | 0                           |
|         | 0.03307   | 0.03066      | 0.0005183              | 0                           |
|         | 0         | 0            | 0                      | 0                           |
| -CHO (C$_7$) | 0.300     | 0.600        | 0.03704                | 0                           |
|         | 0.300     | 0.600        | 0.03704                | 0                           |
|         | 0.300     | 0.600        | 0.03704                | 0                           |
Table S15. Observed and calculated distances with a variety of functionals and basis set for 4-piridinecarboxaldehyde-Cu(II).

| X-ray N-Cu | B3LYP/6-31**G(d,p)/LANL2DZ N-Cu | B3LYP/cc-pVTZ/LANL2DZ N-Cu | PBE0-D3/6-31**G(d,p)/extrabasis for Cu(II) N-Cu | B3PW91/6-31**G(d,p)/LANL2DZ N-Cu | Two step optimization(*) N-Cu |
|------------|----------------------------------|-----------------------------|-----------------------------------------------|---------------------------------|-----------------------------|
| 2.0        | 2.1                              | 2.1                         | 2.1                                           | 2.1                             | 2.1                         |
| 2.0        | 2.6                              | 2.5                         | 2.9                                           | 2.5                             | 2.1                         |
| 2.0        | 2.1                              | 2.1                         | 2.3                                           | 2.1                             | 2.1                         |
| 2.0        | 2.5                              | 2.6                         | 2.0                                           | 2.5                             | 2.1                         |

Table S16. Observed and calculated distances with a variety of functionals and basis set for 3-piridynecarboxaldehyde-Cu(II).

| X-ray N-Co | B3LYP/6-31**G(d,p)/LANL2DZ N-Co | B3LYP/cc-pVTZ/LANL2DZ N-Co | PBE0-D3/6-31**G(d,p)/extrabasis for Cu(II) N-Co | B3PW91/6-31**G(d,p)/LANL2DZ N-Co | Two step optimization(*) N-Co |
|------------|---------------------------------|-----------------------------|-----------------------------------------------|---------------------------------|-----------------------------|
| 2.2        | 2.1                              | 2.1                         | 2.1                                           | 2.1                             | 2.1                         |
| 2.1        | 2.6                              | 2.4                         | 3.0                                           | 2.6                             | 2.1                         |
| 2.1        | 2.5                              | 2.1                         | 2.5                                           | 2.2                             | 2.1                         |
| 2.2        | 2.1                              | 2.6                         | 2.0                                           | 2.5                             | 2.1                         |

*See Experimental Section 4.5 in the manuscript.

Figure S26. Dispersion of values obtained from DFT calculations. Values obtained for the orthoester moiety in the copper complex for the 4-pyridinecarboxaldehyde (left) and for Cu(II)-3-pyridinecarboxaldehyde (right). The numbering corresponds to those in Figures 1 and 2 and the color represents each of the nuclei.
Solid-state NMR results.

Figure S27. 2D $^1$H-$^{13}$C HETCOR spectra for the single crystals obtained with 4-pyridinecarboxaldehyde and CuCl$_2$ in methanol with a contact time of 50 (left) or 500 $\mu$s (right) (MAS rate: 15 kHz).

References:

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(3) Crespi, A. F.; Vega, D.; Chattah, A. K.; Monti, G. A.; Buldain, G. Y.; Lázaro-Martínez, J. M. Gem-Diol and Hemiacetal Forms in Formylpyridine and Vitamin-B6-Related Compounds: Solid-State NMR and Single-Crystal X-Ray Diffraction Studies. *J. Phys. Chem. A* 2016, 120, 7778–7785. https://doi.org/10.1021/acs.jpca.6b07898.