**Supplementary Material for**

# Synthesis, crystal structure and thermal decomposition of Cu(II), Co(II), Mn(II) complexes with hetero-ligands containing cysteic acid, 4,4'-dimethyl-2,2'-bipyridine and azide

Asma Lehleh,[a] Adel Beghidja,[a]* Chahrazed Beghidja,[a] Olivier Mentré,[b] and Richard Welter,[c]*

*[a] Unité de Recherche de Chimie de l'Environnement et Moléculaire Structurale (CHEMS), Université-Mentouri de Constantine, route Aïn elbey 25000 Constantine, Algérie,*

*[b] Université Lille Nord de France. Unité de Catalyse et de Chimie du Solide, CNRS UMR 8181, ENSC Lille – UST Lille, BP 90108, 59652 Villeneuve d'Ascq cedex, France.*

*[c] UMR CNRS 7177, laboratoire Decomet, université de Strasbourg, 4, rue Blaise-Pascal, 67070 Strasbourg cedex, France*

* a_beghidja@yahoo.fr, welter@unistra.fr

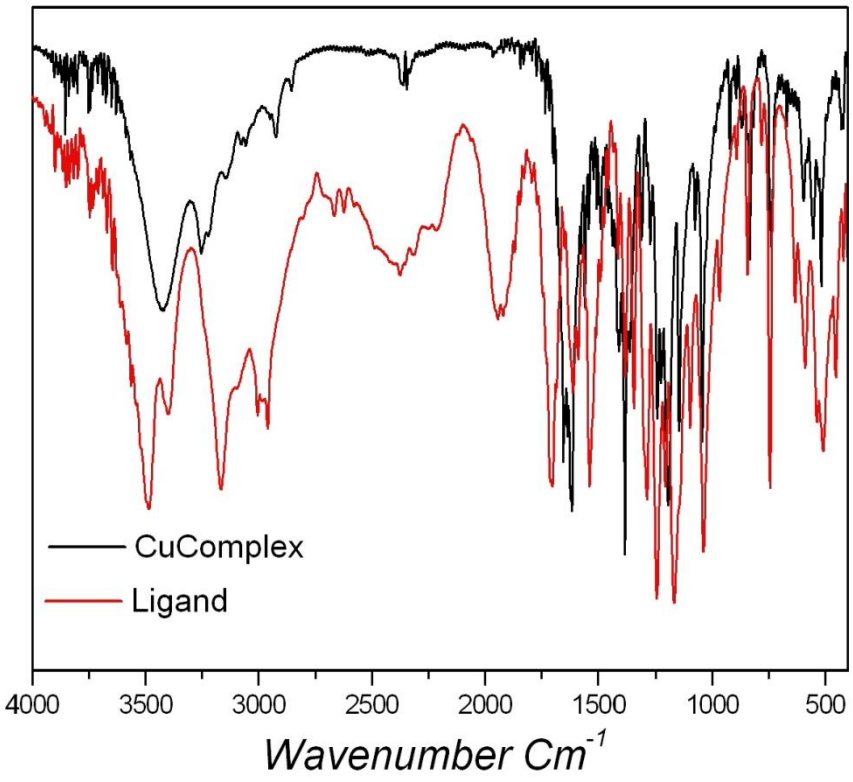


**Fig. S1.** *Infrared spectrum of complex **1** and ligand.*

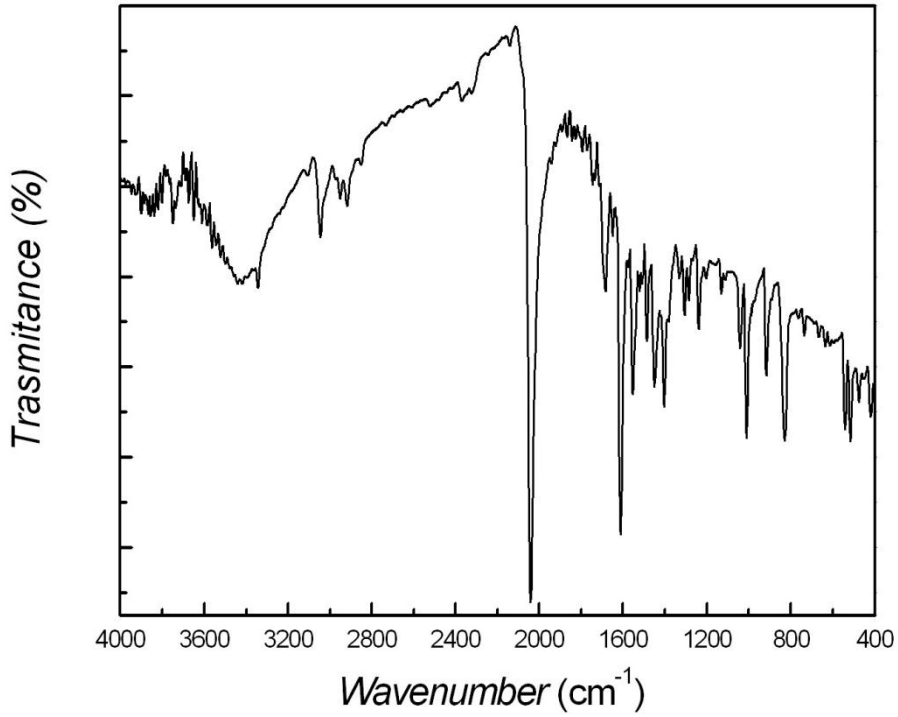

**Fig.S2.** *Infrared spectrum of complex **2**.*

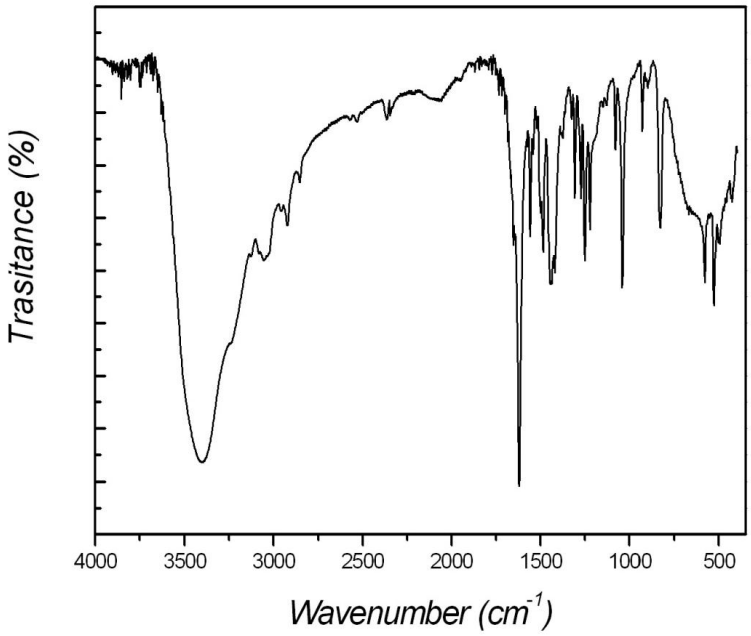


**Fig. S3.** *Infrared spectrum of complex **3**.*

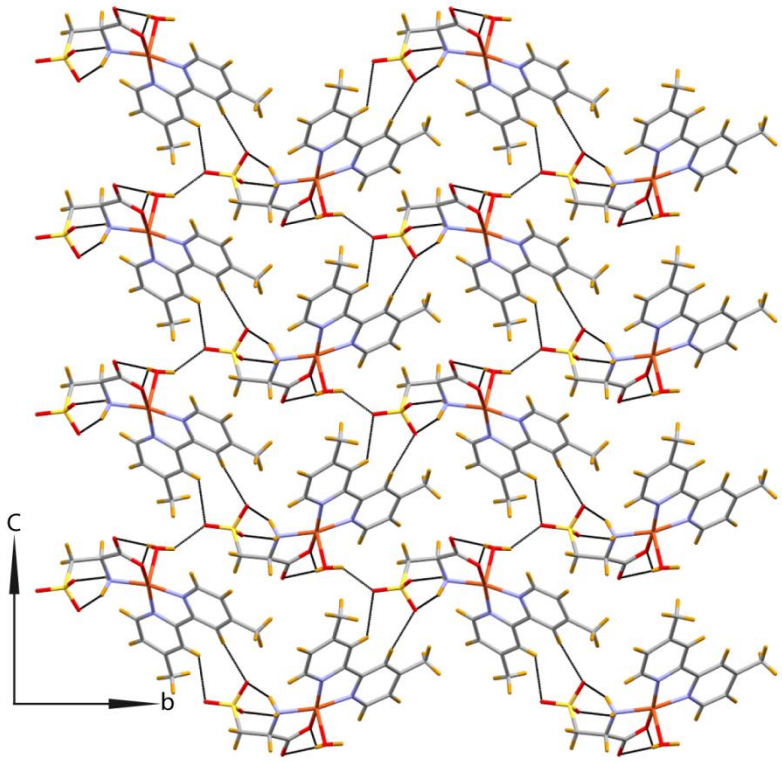


**Fig. S4.** *Mercury view of the crystal structure of **1** along the a-axis showing the three-dimensional network via the hydrogen bonds through C-H...O, N-H...O and O-H...O atoms*

**Table S :** Selected bond lengths (Å) and bond angles (°) of compounds **1-3**.

| **Compound 1** | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cu1 | O1 | 1.950(3) | | S1 | C3 | 1.781(4) | |
| Cu1 | O1W | 2.231(4) | | O1 | C1 | 1.263(4) | |
| Cu1 | N1 | 1.970(4) | | O2 | C1 | 1.227(5) | |
| Cu1 | N2 | 1.989(3) | | N1 | C2 | 1.478(5) | |
| Cu1 | N3 | 2.004(3) | | N2 | C8 | 1.349(4) | |
| S1 | O3 | 1.440(3) | | N2 | C4 | 1.340(4) | |
| S1 | O4 | 1.424(3) | | N3 | C13 | 1.343(4) | |
| S1 | O5 | 1.425(3) | | N3 | C9 | 1.356(4) | |
| O1 | Cu1 | O1W | 93.48(11) | Cu1 | O1 | C1 | 116.2(2) |
| O1 | Cu1 | N1 | 83.75(11) | Cu1 | N1 | C2 | 108.7(2) |
| O1 | Cu1 | N2 | 94.05(10) | C4 | N2 | C8 | 118.5(3) |
| O1 | Cu1 | N3 | 164.96(11) | Cu1 | N2 | C8 | 115.1(2) |
| O1W | Cu1 | N1 | 91.92(13) | Cu1 | N2 | C4 | 126.4(2) |
| O1W | Cu1 | N2 | 102.96(12) | C9 | N3 | C13 | 118.0(3) |
| O1W | Cu1 | N3 | 101.52(11) | Cu1 | N3 | C13 | 127.6(2) |
| N1 | Cu1 | N2 | 165.08(12) | N2 | C4 | C5 | 121.9(3) |
| N1 | Cu1 | N3 | 96.83(12) | Cu1 | N3 | C9 | 114.43(19) |
| N2 | Cu1 | N3 | 81.51(11) | O2 | C1 | C2 | 119.9(3) |
| O3 | S1 | O4 | 111.3(2) | O1 | C1 | O2 | 124.6(3) |
| O3 | S1 | O5 | 111.9(2) | O1 | C1 | C2 | 115.5(3) |
| O3 | S1 | C3 | 106.69(18) | N1 | C2 | C3 | 111.7(3) |
| O4 | S1 | O5 | 113.0(2) | N1 | C2 | C1 | 110.1(3) |
| O4 | S1 | C3 | 108.11(18) | S1 | C3 | C2 | 115.8(2) |
| O5 | S1 | C3 | 105.5(2) | | | | |
| **Compound 2** | | | | | | | |
| Mn1 | Cl1 | 2.4569(15) | | N2 | C10 | 1.337(3) | |
| Mn1 | N1 | 2.314(2) | | N3 | C13 | 1.338(3) | |
| Mn1 | N2 | 2.262(2) | | N3 | C17 | 1.345(3) | |
| Mn1 | N3 | 2.271(2) | | N4 | C18 | 1.343(3) | |
| Mn1 | N4 | 2.313(2) | | N4 | C22 | 1.336(4) | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Mn1 | N5 | 2.173(3) | | N5 | N6 | 1.109(4) | |
| N1 | C1 | 1.342(3) | | N6 | N7 | 1.191(4) | |
| N1 | C5 | 1.349(3) | | N2 | C6 | 1.343(3) | |
| | | | | | | | |
| Cl1 | Mn1 | N1 | 168.74(5) | Mn1 | N2 | C6 | 118.91(15) |
| Cl1 | Mn1 | N2 | 97.47(6) | Mn1 | N2 | C10 | 122.81(16) |
| Cl1 | Mn1 | N3 | 93.16(6) | C6 | N2 | C10 | 118.13(19) |
| Cl1 | Mn1 | N4 | 89.44(6) | Mn1 | N3 | C13 | 121.86(18) |
| Cl1 | Mn1 | N5 | 97.51(8) | Mn1 | N3 | C17 | 116.29(15) |
| N1 | Mn1 | N2 | 71.39(7) | Mn1 | N4 | C18 | 116.29(16) |
| N1 | Mn1 | N3 | 97.05(7) | Mn1 | N4 | C22 | 126.51(18) |
| N1 | Mn1 | N4 | 89.21(7) | C18 | N4 | C22 | 117.2(2) |
| N1 | Mn1 | N5 | 86.27(9) | Mn1 | N5 | N6 | 125.9(2) |
| N2 | Mn1 | N3 | 160.35(8) | N5 | N6 | N7 | 178.8(4) |
| N2 | Mn1 | N4 | 91.61(7) | N1 | C1 | C2 | 123.3(2) |
| N2 | Mn1 | N5 | 99.45(8) | C13 | N3 | C17 | 117.2(2) |
| N3 | Mn1 | N4 | 71.95(7) | Mn1 | N1 | C1 | 125.16(16) |
| N3 | Mn1 | N5 | 95.48(9) | Mn1 | N1 | C5 | 117.33(15) |
| N4 | Mn1 | N5 | 166.02(9) | C1 | N1 | C5 | 117.5(2) |
| **Compound 3** | | | | | | | |
| Co1 | N1 | 1.937(3) | | N1 | C1 | 1.357(4) | |
| Co1 | N2 | 1.947(3) | | N1 | C5 | 1.356(4) | |
| Co1 | N3 | 1.930(3) | | N2 | C6 | 1.349(4) | |
| Co1 | N4 | 1.936(3) | | N2 | C10 | 1.350(4) | |
| Co1 | N5 | 1.925(3) | | N3 | C17 | 1.354(4) | |
| Co1 | N6 | 1.925(3) | | N3 | C13 | 1.357(4) | |
| Co2 | Cl1 | 2.2982(16) | | N4 | C18 | 1.362(4) | |
| Co2 | Cl2 | 2.267(2) | | N4 | C22 | 1.347(4) | |
| Co2 | Cl3 | 2.2790(17) | | N5 | C29 | 1.363(4) | |
| Co2 | Cl4 | 2.258(2) | | N5 | C25 | 1.350(4) | |
| N6 | C30 | 1.348(4) | | N6 | C34 | 1.351(4) | |
| | | | | | | | |
| N1 | Co1 | N2 | 83.20(10) | Co1 | N1 | C5 | 114.5(2) |
| N1 | Co1 | N3 | 87.71(10) | Co1 | N1 | C1 | 127.4(2) |
| N1 | Co1 | N4 | 93.59(11) | C1 | N1 | C5 | 118.2(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N1 | Co1 | N5 | 93.93(10) | Co1 | N2 | C10 | 127.9(2) |
| N1 | Co1 | N6 | 176.20(11) | C6 | N2 | C10 | 118.0(3) |
| N2 | Co1 | N3 | 94.12(11) | Co1 | N2 | C6 | 114.2(2) |
| N2 | Co1 | N4 | 175.98(11) | Co1 | N3 | C17 | 114.6(2) |
| N2 | Co1 | N5 | 89.23(10) | C13 | N3 | C17 | 118.1(3) |
| N2 | Co1 | N6 | 94.00(11) | Co1 | N3 | C13 | 127.3(2) |
| N3 | Co1 | N4 | 83.32(10) | C18 | N4 | C22 | 118.4(3) |
| N3 | Co1 | N5 | 176.43(11) | Co1 | N4 | C22 | 127.4(2) |
| N3 | Co1 | N6 | 95.08(11) | Co1 | N4 | C18 | 114.1(2) |
| N4 | Co1 | N5 | 93.40(10) | Co1 | N5 | C29 | 114.7(2) |
| N4 | Co1 | N6 | 89.31(11) | Co1 | N5 | C25 | 127.3(2) |
| N5 | Co1 | N6 | 83.43(10) | C25 | N5 | C29 | 117.9(3) |
| Cl3 | Co2 | Cl4 | 109.85(6) | Co1 | N6 | C34 | 126.7(2) |
| Cl1 | Co2 | Cl4 | 110.04(7) | Co1 | N6 | C30 | 114.5(2) |
| Cl1 | Co2 | Cl2 | 113.69(6) | C30 | N6 | C34 | 118.8(3) |
| Cl1 | Co2 | Cl3 | 106.53(5) | Cl2 | Co2 | Cl3 | 110.20(6) |
| Cl2 | Co2 | Cl4 | 106.54(6) | | | | |

**Table 3** Hydrogen bond parameters determined by the PLATON software for compounds **1-3**

| **D** | **H** | **A** | **D - H** | **H...A** | **D...A** | **D - H...A** |
|---|---|---|---|---|---|---|
| **Compound 1** | | | | | | |
| N1 | H1A | O4 #1 | 0.9000 | 2.1100 | 2.816(5) | 135.00 |
| N1 | H1B | O3 | 0.9000 | 2.0900 | 2.846(5) | 141.00 |
| O1W | H1W | O5 #2 | 0.853(16) | 2.04(3) | 2.753(5) | 141(4) |
| O1W | H2W | O1 #1 | 0.85(3) | 2.42(3) | 3.112(5) | 140(3) |
| O1W | H2W | O2 #1 | 0.85(3) | 2.14(3) | 2.936(5) | 156(3) |
| C4 | H4 | O1 | 0.9300 | 2.5900 | 3.067(5) | 113.00 |
| C7 | H7 | O3 #3 | 0.9300 | 2.4300 | 3.309(5) | 158.00 |
| C10 | H10 | O5 #3 | 0.9300 | 2.5200 | 3.168(6) | 127.00 |

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

| **Compound 2** | | | | | | |
|---|---|---|---|---|---|---|
| C4 | H4 | Cl1 #1 | 0.9500 | 2.7800 | 3.710(3) | 166.00 |
| C21 | H21 | Cl1 #2 | 0.9500 | 2.8100 | 3.632(4) | 145.00 |
| C23 | H23C | Cl1 #3 | 0.9800 | 2.7900 | 3.683(4) | 151.00 |
| **Symmetry Code :** #1 : x,1/2-y,-1/2+z ; #2 : -x,1-y,1-z ; #3 : 1+x,1/2-y,1/2+z | | | | | | |
| **Compound 3** | | | | | | |
| O1W | H11 | O4W | 0.8500 | 2.4000 | 2.881(5) | 116.00 |
| O1W | H12 | Cl2 | 0.8500 | 2.4500 | 3.233(4) | 152.00 |
| O2W | H21 | Cl3 #1 | 0.8500 | 2.5600 | 3.303(5) | 147.00 |
| O3W | H32 | O4W | 0.8400 | 2.0200 | 2.845(6) | 168.00 |
| O4W | H42 | O1W | 0.8600 | 2.0400 | 2.881(5) | 166.00 |
| O5W | H51 | Cl5#2 | 0.8500 | 2.7000 | 3.385(13) | 138.00 |
| O6W | H62 | Cl5 #3 | 0.8500 | 2.7000 | 3.200(4) | 119.00 |
| O7W | H71 | Cl1#4 | 0.8500 | 2.4100 | 3.247(4) | 169.00 |
| O7W | H72 | O2W | 0.8500 | 1.9300 | 2.729(5) | 155.00 |
| C1 | H1 | N4 | 0.9300 | 2.5100 | 3.007(4) | 113.00 |
| C2 | H2 | O6W #5 | 0.9300 | 2.5900 | 3.497(5) | 165.00 |
| C7 | H7 | Cl4 #2 | 0.9300 | 2.6700 | 3.585(4) | 169.00 |
| C9 | H9 | O7W #6 | 0.9300 | 2.5700 | 3.372(5) | 144.00 |
| C10 | H10 | N6 | 0.9300 | 2.5500 | 3.033(5) | 113.00 |
| C13 | H13 | N2 | 0.9300 | 2.5300 | 3.022(4) | 113.00 |
| C19 | H19 | Cl1 #5 | 0.9300 | 2.7100 | 3.633(4) | 171.00 |
| C22 | H22A | N5 | 0.9300 | 2.5000 | 2.992(4) | 113.00 |
| C25 | H25 | N1 | 0.9300 | 2.5100 | 3.008(5) | 114.00 |
| C33 | H33 | Cl2 #3 | 0.9300 | 2.8100 | 3.680(4) | 157.00 |
| C34 | H34 | N3 | 0.9300 | 2.5200 | 3.023(5) | 114.00 |
| C35 | H35A | Cl4 #7 | 0.9600 | 2.7200 | 3.507(6) | 139.00 |
| **Symmetry Code :** #1 : x,1/2-y,-1/2+z ; #2 : x,-1/2-y,1/2+z ; #3 :-1+x,y,z ; #4 : 2-x,-1/2+y,1/2-z ; #5 : 1-x,-1/2+y,1/2-z ; #6 : -1+x,1/2-y,1/2+z ; #7 : 1-x,1-y,1-z | | | | | | |