



Full paper/Mémoire

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

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ABSTRACT

Three new transition metal complexes, [Cu(L-cyst)(dmbpy)(H₂O)] (**1**), [Mn(dmbpy)₂(N₃)(Cl)] (**2**) and [Co(dmbpy)₃].[CoCl₄].Cl.7H₂O (**3**) with (L-cyst = L-cysteic acid, dmbpy = 4,4'-dimethyl-2,2'-bipyridine, N₃ = azide) have been synthesized and characterized by elemental analysis, thermal analysis (DTA/TGA), IR spectroscopy and single crystal X-ray diffraction (XRD). In the complex **1**, the copper atoms are five-coordinated in a distorted square pyramidal site. It forms monomeric species, which are further connected into a three-dimensional supramolecular network through hydrogen bonding interactions. In the complex **2**, the manganese atoms have a distorted octahedral environment with four nitrogen atoms of the two **dmbpy**, one nitrogen atom provided from azide ligand, the coordination sphere being completed by a chlorine atom. (**2**) is also a monomeric complex and the molecular structure of compound **2** is stabilized by non standard weak C-H...Cl hydrogen-bonds. The asymmetric unit of the complex **3** is built of two cobalt-containing fragments: the cationic [Co^{II}(dmbpy)₃]⁺² and the anionic (Co^{II}Cl₄)⁻² groups. The molecular structure of compound **3** is stabilized by hydrogen bonds via O-H...O, O-H...Cl and C-H...Cl interactions. The thermal decompositions for **1** and **3** in the temperature range 30–1000 °C has revealed that the Cu complex decomposes in three steps whereas Co complex decomposes in four steps and transforms into the corresponding metal oxide.

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1. Introduction

The design of new multifunctional materials, combining magnetism and non-linear optical activity [1], magnetism and photo-reactivity [2,3] or magnetism and transport properties [4–7], is currently a challenging field of research for molecular chemists, material chemists and physicists. Metal complexes containing bipyridine and

analogous ligands such as phenanthroline are commonly used in the formation of different complexes with a general variety of transition metals, [8–10] because of their versatile roles at several levels, such as: building blocks for the synthesis of metallo-dendrimers, molecular scaffolding for supramolecular assemblies, in analytical chemistry, in catalysis, in electrochemistry, in the ring-opening metathesis polymerization and biochemistry [11–26]. Such studies are important for better understanding of electron transfer processes, magnetic coupling and magnetic transitions, photochemistry [27–31]. Additionally, owing to an extended π -system, non-covalent π -interactions in biological processes can be mimicked [32].

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Azido-bridged complexes have been focused on for molecular magnetism for many years because azide ions have two possible bridging modes: end-to-end (EE) with preferred antiferromagnetic interactions and end-on (EO) with preferred ferromagnetic interactions. However carboxylate-bridged complexes continue to be much investigated due to their interesting coordination chemistry allowing for unusual structural features, leading to various physical and chemical properties (dyes, extractants, drugs, pesticides, catalysts) [33–40]. Indeed, in most cases, it is still difficult to predict the exact structures and compositions of the product of the mixed ligands [41]. As a continuation of our researches on the synthesis of new chiral inorganic coordination complexes using α -hydroxy carboxylates [42–46], we report in this paper the synthesis and crystal structure of three new complexes using α -amino carboxylates (L-cysteic acid) with mixed ligands (dmbpy “4,4'-dimethyl-2,2'-bipyridine”, N_3 “azide”, the $\text{Cu}(\text{L-cyst})(\text{dmbpy})\cdot\text{H}_2\text{O}$ (**1**), $\text{cis}[\text{Mn}(\text{N}_3)\text{Cl}(\text{dmbpy})_2]$ (**2**) and $[\text{Co}(\text{dmbpy})_3][\text{CoCl}_4]\cdot 7\text{H}_2\text{O}\cdot\text{Cl}$ (**3**).

Only few results have been reported on complexes involving the cysteic acid ((S)-2-amino-3-sulfopropionic acid) (Scheme 1) [47–51]. It can adopt several coordination modes: monodentate, bidentate, tridentate and tetradentate. Scheme 2 shows the different coordination modes of cysteic acid with the corresponding references.

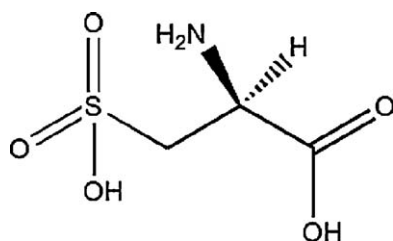
2. Experimental

2.1. Materials

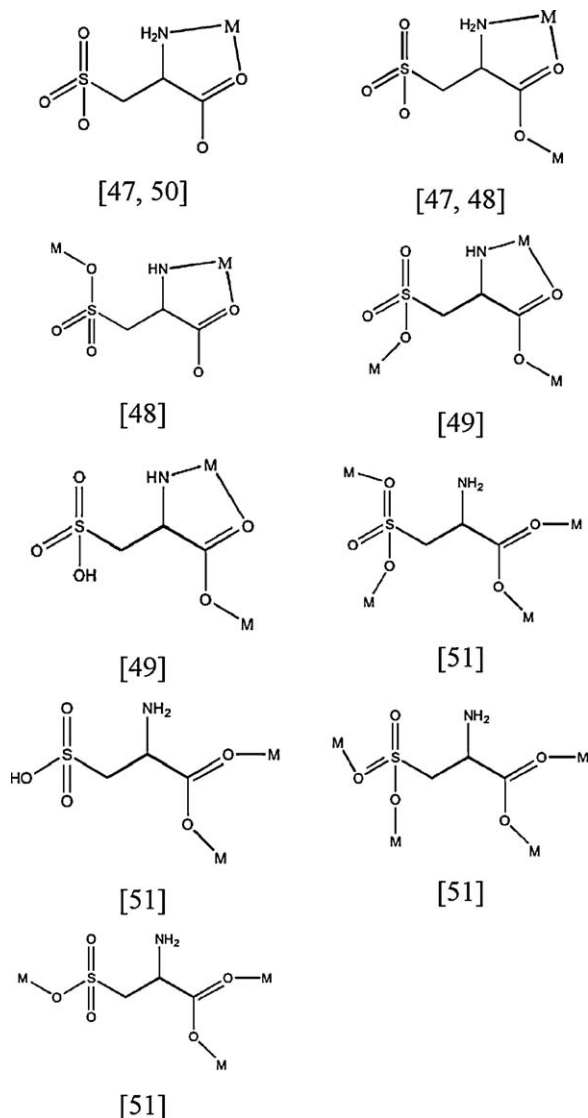
L-Cysteic acid ((S)-2-amino-3-sulfopropionic acid), 4,4'-dimethyl-2,2'-bipyridine, sodium azide, $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$, $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ were purchased from Alfa Aesar. All the reagents and solvents were used as received without further purification. The complexes were obtained at room temperature using a general procedure described below.

2.2. Physical measurement

Elemental C, H, N, and S analyses were performed by the ‘Service de Microanalyses’ of the Institut Le Bel and of the Institut Charles-Sadron (Université de Strasbourg, France). FT-IR studies were performed with an ATI Mattson Genesis computer-driven instrument (0.1 mm thick powder samples in KBr). Thermogravimetric experiments were performed using a Setaram TG92 instrument (heating rate of 5°C min^{-1} , air stream) [heating in air from 30°C to 1000°C at 5°C min^{-1} , 30 min at 1000°C to transform into the



Scheme 1. (S)-2-amino-3-sulfopropionic acid ((S)-cysteic acid).



Scheme 2. Coordination modes of (S)-2-amino-3-sulfopropionic acid ((S)-cysteic acid).

corresponding metal oxide (the nature of which was checked by X-ray powder diffraction) and cooling to 30°C at $10^\circ\text{C min}^{-1}$. Crystal structures were determined using a NONIUS Kappa CCD diffractometer equipped with graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$).

2.3. Synthesis of the complexes

2.3.1. Synthesis of $[\text{Cu}(\text{L-cyst})(\text{dmbpy})\cdot\text{H}_2\text{O}]$ (**1**)

A methanolic solution containing $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ (0.241 g, 1 mmol) and 4,4'-dimethyl-2,2'-bipyridine (0.186 g, 1 mmol) was added with stirring to a methanolic solution containing L-cysteic acid (0.187 g, 1 mmol) and sodium azide (0.195 g, 3 mmol). After few minutes a blue green precipitate appears and was filtrated (after recrystallization of this precipitate by slow evaporation of

methanol as solvent, we obtain the product **1**). A diluted clear blue solution of the complex in methanol solution was left at room temperature. After several days, X-ray qualified blue single crystals were grown, which were filtrated and characterized (yield: 0.31 g, 71.6% on the basis of $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}]$). Anal. Calc. for $\text{C}_{15}\text{H}_{19}\text{CuN}_3\text{O}_6\text{S}$: C: 41.61; H: 4.42; N: 9.70, S: 7.40%. Found: C: 42.01 H: 3.98; N: 9.39; S: 7.72%.

2.3.2. Synthesis of $[\text{Mn}(\text{dmbpy})_2(\text{N}_3)\text{Cl}]$ (**2**)

A methanolic solution containing $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.1 g, 0.5 mmol) and sodium azide (0.098 g, 1.5 mmol) and L-cysteic acid (0.094 g, 0.5 mmol) was stirred for 30 min, and then a methanol solution containing 4,4'-dimethyl-2,2'-bipyridine (0.093 g, 0.5 mmol) was added. After few minutes a beige precipitate appears and was filtrated while the solution was left at room temperature. After one month, orange single crystals suitable for XRD-analysis were obtained, which were filtrated and characterized (yield: 0.09 g, 35.92% on the basis of $[\text{MnCl}_2 \cdot 4\text{H}_2\text{O}]$). Anal. Calc. for $\text{C}_{24}\text{H}_{24}\text{ClMnN}_7$: C, 57.54; H, 4.82; N, 19.57. Found: C, 56.84; H, 4.37; N, 20.02%.

2.3.3. Synthesis of $[\text{Co}(\text{dmbpy})_3][\text{CoCl}_4] \cdot 7\text{H}_2\text{O} \cdot \text{Cl}$ (**3**)

A methanolic solution containing cobalt (II) chloride hexahydrate (0.119 g, 0.5 mmol) and 4,4'-dimethyl-2,2'-bipyridine (0.093 g, 0.5 mmol) was added with stirring to a methanol solution containing L-cysteic acid (0.094 g, 0.5 mmol) and sodium azide (0.033 g, 0.5 mmol). After few minutes a red-brown precipitate appears, and which filtrated then the clear solution was left at room temperature. After few weeks, X-ray qualified green single crystals were obtained, which were filtrated and characterized (yield: 0.20 g, 41.06% on the basis of $[\text{CoCl}_2 \cdot 6\text{H}_2\text{O}]$). Anal. Calc. for $\text{C}_{36}\text{H}_{50}\text{Co}_2\text{N}_6\text{O}_7\text{Cl}_5$: C: 44.39; H: 5.17; N: 8.62%. Found: C: 44.71; H: 4.92; N: 8.92%.

CAUTION: Although not encountered in our experiments, azido compounds of metal ions are potentially explosive. Only a small amount of the materials should be prepared, and it should be handled with care.

2.4. X-ray diffraction studies

Single crystals of the complexes **1**, **2**, **3** were mounted on a Nonius Kappa-CCD area detector diffractometer, Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), using $\omega-2\theta$ scans at room temperature. The parameters of the data collection (Denzo software) [52] and structure refinements are given in the Table S. The structures were solved using direct methods (SHELXS97) and refined against F^2 using the SHELXL97 and CRYSTALBUILDER softwares [53,54]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereo-chemistry and refined using a riding model in SHELXL97. The absorption was not corrected (small and almost isotropic crystal-shapes). Table S gives crystallographic crystal data and final refinement parameters for the complexes **1**, **2** and **3**. Selected bond lengths and angles are given in corresponding figure captions. Geometrical calculations were carried out with PLATON [55].

3. Results and discussion

3.1. Crystal and molecular structure of $[\text{Cu}(2,2'\text{-dmbpy})(\text{L-cyst})(\text{H}_2\text{O})]$ (**1**)

The asymmetric units of **1**, **2** and **3** with the atom-numbering schemes are illustrated in Figs. 1, 4 and 6, respectively. The complex **1** crystallizes in the monoclinic system with chiral space group $P2_1$, contrary to what has been observed on a similar compound namely of $[\text{Cu}(2,2'\text{-bpy})(\text{L-cyst})(\text{H}_2\text{O})]$ published recently where the structure is centrosymmetric [47]. The Cu(II) ion is coordinated by one 2,2'-dmbpy molecule acting as a bidentate ligand (through the two nitrogen atoms (N2, N3)), and one L-cys moiety (through the oxygen and nitrogen atoms (O1, N1)). The geometry around the metal is a distorted square pyramidal with a water molecule lying in the axial position through O1W. The basal plan is formed by (O1, N1, N2, N3) where the central metal atom is slightly above it (0.255(3) Å). This deviation is longer than observed in $\text{Cu}(2,2'\text{-bpy})(\text{L-cyst})(\text{H}_2\text{O})$ ($\approx 0.13 \text{ \AA}$). The Cu-N distances of the dmbpy and the amino nitrogen atoms of the L-cys ligand range from 1.970(4) to 2.004(3) Å, while the Cu-O distance of the carboxylate oxygen coordinated to the metal is 1.950(3) Å and the distance Cu-O of the coordinated water molecule is 2.231(4) Å, close to the distances observed in $\text{Cu}(\text{bpy})(\text{L-cyst})(\text{H}_2\text{O})$ [47]. The packing diagram and hydrogen bonding interactions scheme were analyzed by PLATON software, the packing and hydrogen bonding interactions viewed down the a-axis are shown in Fig. 2. The crystal structure can be described as chains that develops in a zigzag pattern along the b-axis via weak hydrogen bonds type C-H...O between C7-H7...O3 and C10-H10...O5. These chains are interconnected along the c-axis to form a sheet through medium hydrogen bonds via O-H...O between atoms O1W-H1W...O5 (Fig. S4), these sheets are also interconnected along c-axis by medium hydrogen bond type N-H...O and O-H...O through N1-H7A...O4, O1W-H2W...O1 and O1W-H2W...O2.

In addition to these hydrogen interactions, we also note that the cohesion in the crystal is ensured by weak interactions type $\pi \dots \pi$ stacking, observed between centroid (Cg1) of the N2-C8 pyridil ring and the centroid (Cg2) of the N3-C13 pyridil ring of the adjacent molecule, with a Cg1...Cg2 distance of 3.765(3) Å (Fig. 3) [47]. The racemic mixture in the crystal structure is then not observed, on the contrary to what has been observed for complexes described with the cysteic acid and 2,2' bpy [47,48,50].

3.2. Crystal and molecular structure of $[\text{Mn}(2,2'\text{-dmbpy})_2(\text{N}_3)\text{Cl}]$ (**2**)

An ORTEP view of the molecular structure of complex **2** in the crystal is depicted in Fig. 4. The manganese(II) ion is surrounded by two cis-coordinated dmbpy ligand, coordinated by nitrogen atoms (N1, N2) of the first ligand (Mn1-N1 = 2.315(2) Å, Mn1-N = 2.2261(2) Å) and the atoms (N3, N4) for the second ligand (Mn1-N3 = 2.270(2) Å, Mn1-N4

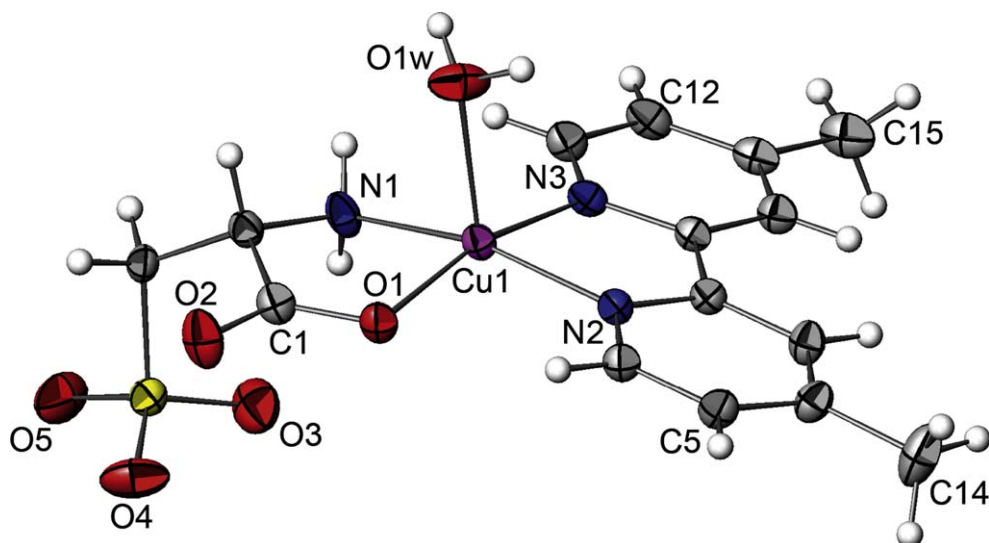


Fig. 1. ORTEP view (ATOMS software) of **1** ($\text{Cu}^{\text{II}}(\text{L-cyst})(\text{dmbpy})(\text{H}_2\text{O})$) with partial labeling scheme. The ellipsoids enclose 50% of the electronic density. Selected distances (Å) and angles ($^\circ$): Cu1–O1 = 1.950(3), Cu1–O1w = 2.231(4), Cu1–N1 = 1.970(4), Cu1–N2 = 1.989(3), Cu1–N3 = 2.004(3), S1–O3 = 1.440(3), S1–O4 = 1.424(3), S1–O5 = 1.425(3), S1–C3 = 1.781(4), O1–C1 = 1.263(4), O2–C1 = 1.227(5), N1–C2 = 1.478(5), N2–C8 = 1.349(4), N2–C4 = 1.340(4), N3–C13 = 1.343(4), N3–C9 = 1.356(4), O1–Cu1–O1w = 93.48(11), O1–Cu1–N1 = 83.75(11), O1–Cu1–N2 = 94.05(10), O1–Cu1–N3 = 164.96(11), N1–Cu1–N2 = 165.08(12), O3–S1–O4 = 111.3(2), O3–S1–O5 = 111.9(2).

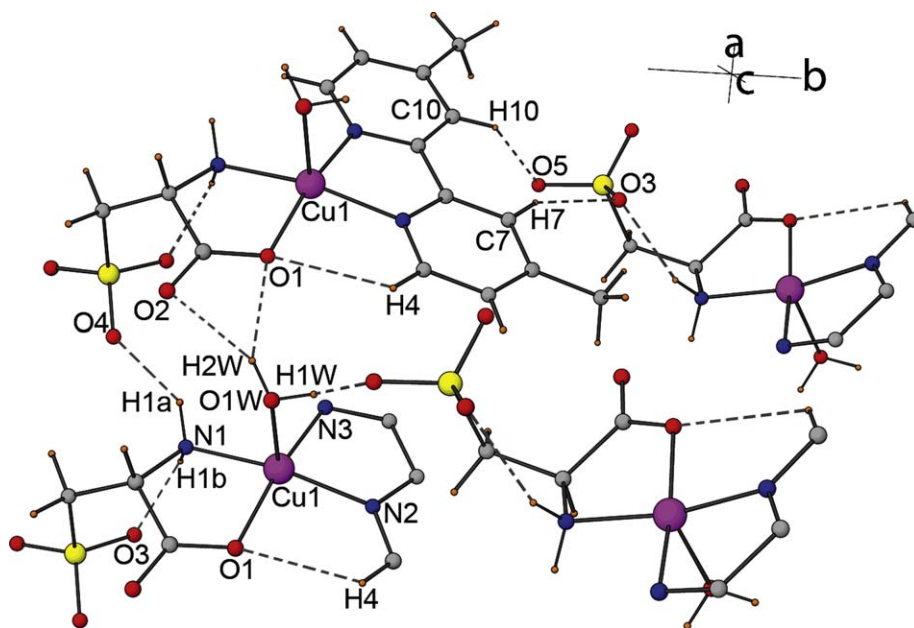


Fig. 2. Partial view of a selected part of the crystal structure of **1** showing hydrogen bonds. Dashed lines indicate inter- and intramolecular H-bonds.

2.312(2) Å), and the N5 atom provided by the azide ligand (Mn1–N5 = 2.174(3) Å), the coordinated sphere is completed by the chlorine anion Cl1 (Mn1–Cl1 = 2.4567(15) Å). The coordination is a distorted octahedral, with an irregular equatorial (N2–N3–N4–N5) plane.

The molecular structure of complex **2** is stabilized by non standard weak hydrogen-bonds. In fact, C–H...Cl intermolecular hydrogen bonds are observed via C(4)–H(4)...Cl(1), C(21)–H(21)...Cl(1) and C(23)–H(23)...Cl(1).

The dihedral angle between the pyridil rings of the first dmbpy ligand is 22.24(5) $^\circ$, and 3.95(4) $^\circ$ for the second dmbpy ligand (Fig. 5).

3.3. Crystal and molecular structure of $[\text{Co}(\text{dmbpy})_3][\text{CoCl}_4] \cdot 7(\text{H}_2\text{O}) \cdot (\text{Cl})$ (**3**)

The crystal structure of **3** is composed of $[\text{Co}(\text{dmbpy})_3]^{2+}$ cation, $[\text{CoCl}_4]^{2-}$ anions, uncoordinated

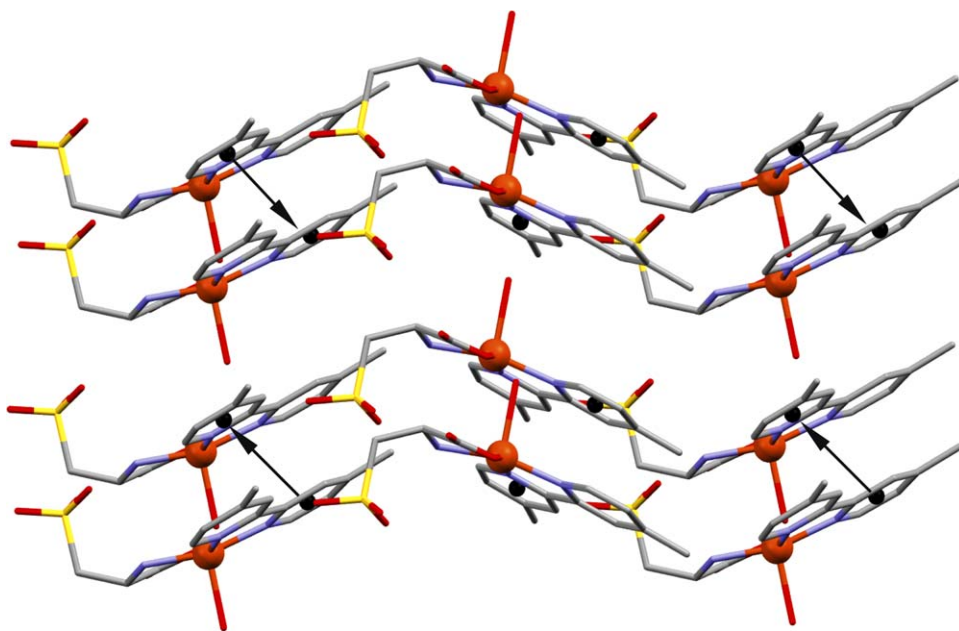


Fig. 3. Partial view of the crystal structure of **1** showing $\pi \dots \pi$ stacking interactions.

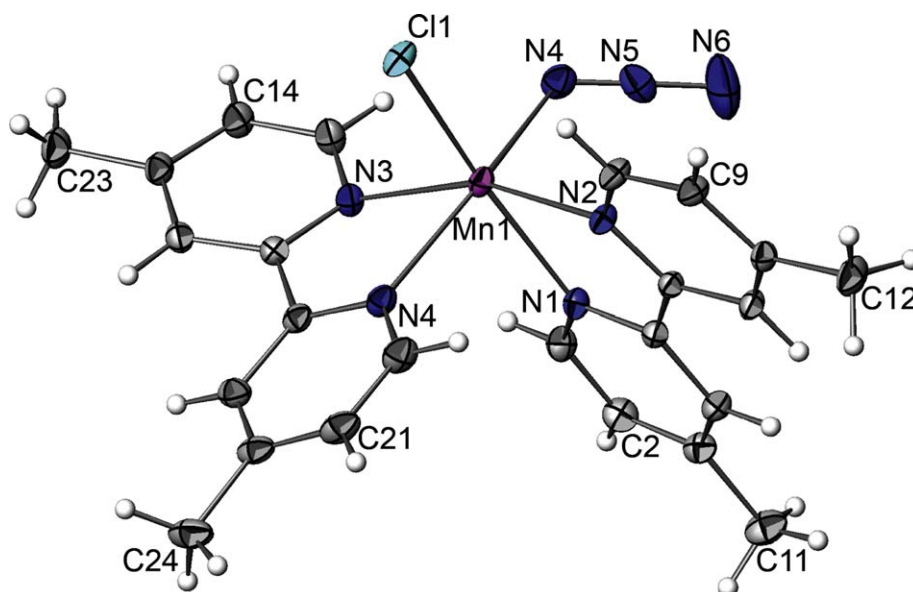


Fig. 4. ORTEP view (ATOMS software) of **2** ($\text{Mn}^{\text{II}}(\text{dmbpy})_2(\text{N}_3)(\text{Cl})$) with partial labeling scheme. The ellipsoids enclose 50% of the electronic density. Selected distances (Å) and angles ($^\circ$): Mn1 Cl1 = 2.4569(15), Mn1-N1 = 2.314(2), Mn1-N2 = 2.262(2), Mn1-N3 = 2.271(2), Mn1-N4 = 2.313(2), Mn1-N5 = 2.173(3), N1-C1 = 1.342(3), N1-C5 = 1.349(3), N2-C6 = 1.343(3), N2-C10 = 1.337(3), N3-C13 = 1.338(3), N3-C17 = 1.345(3), N4-C18 = 1.343(3), N4-C22 = 1.336(4), N5-N6 = 1.109(4), N6-N7 = 1.191(4), Cl1-Mn1-N1 = 168.74(5), Cl1-Mn1-N3 = 93.16(6), Cl1-Mn1-N4 = 89.44(6), N1-Mn1-N2 = 71.39(7), N2-Mn1-N3 = 160.35(8), N3-Mn1-N4 = 71.95(7), N3-Mn1-N5 = 95.48(9), N4-Mn1-N5 = 166.02(9), N5-N6-N7 = 178.8(4).

Cl^- anion and seven solvation water molecules; one is an hydronium cation (H_3O^+) (Fig. 6). The cobalt atom of the cation (Co1) is coordinated to six nitrogen atoms (N1; N2; N3; N4; N5; N6) which belong to three different bipyridyl ligands forming a distorted octahedron. The Co1–N distance range from 1.925(3)–1.947(3)Å, and dmbpy rings are planar, while the $[\text{CoCl}_4]$ anion, exhibit tetrahedral

geometry, with the Co(2) ion surrounded by four Cl atoms, with Cl–Co–Cl angles ranging from 106.53 (4) to 113.69 (3) $^\circ$. The mean Co–Cl bond length, 2.27 (7) Å, is close to those observed in similar complexes [57–61].

The structure is stabilized by an extensive network of O–H...O, O–H...Cl and C–H...Cl hydrogen bond interactions [Supplementary material]. The cation [Co

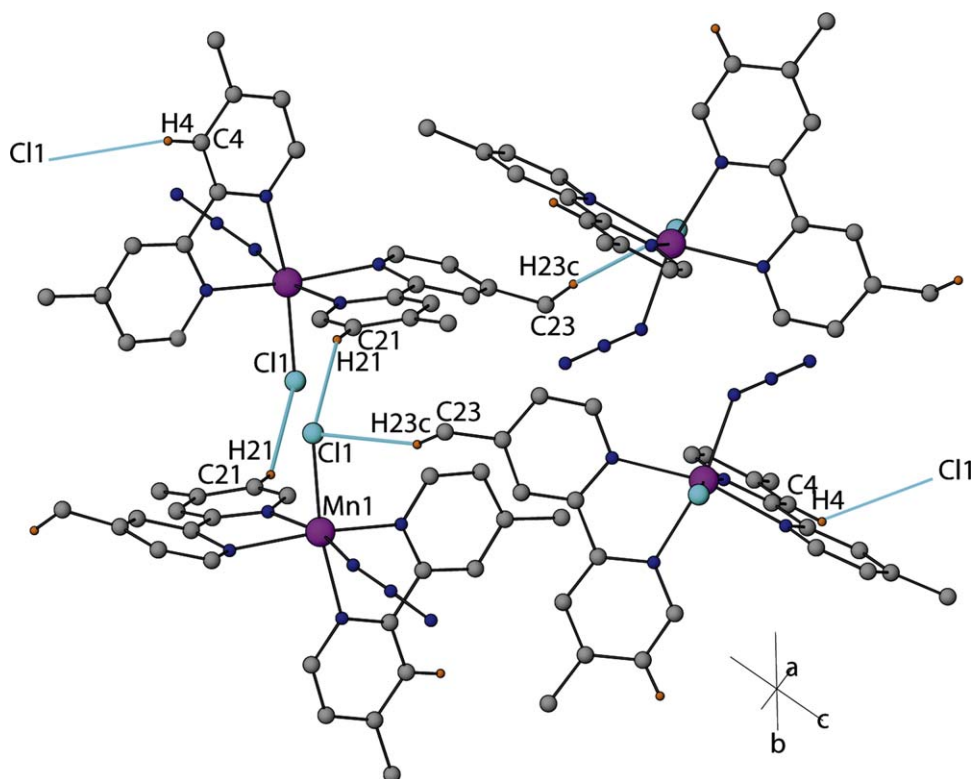


Fig. 5. Partial view of the crystal structure of **2** showing the three-dimensional network of the hydrogen bonds (in green) via C-H...Cl atoms.

(dmbpy)₃²⁺ interacts with the [CoCl₄]²⁻ anion and two water molecules (O6W; O7W) through intermolecular weak hydrogen bonds type C–H...Cl and C–H...O respectively through C2–H2...O6W, C9–H9...O7W, C7–H7...Cl4, C19–H19...Cl1, C33–H33...Cl2 and C35–H35A...Cl4 as shown in Fig. 6. However, the water molecules' hydrogens are involved in intermolecular O–H...Cl interactions with the two anion [CoCl₄]²⁻; Cl⁻ via Cl1–H71...O7W, Cl2–H12...O1W, Cl3–H21...O2W and Cl5–H62...O6W as shown in Fig. 7. We also note the presence of weak C–H... π interactions between the centroid (Cg1) of the N2–C10 pyridil ring and H12A (3.657(6)Å; 99.86(2)°), and also between the centroid (Cg2) of the N6–C34 pyridil ring and H12A (3.852(7)Å; 107.08(2)°).

3.4. Spectroscopic properties

The IR spectrum for compound **1** exhibits characteristic bands of the cysteate. The frequency difference between the symmetrical ($\nu_{\text{CO}_{\text{sym}}} = 1384 \text{ cm}^{-1}$) and antisymmetrical ($\nu_{\text{CO}_{\text{asym}}} = 1616 \text{ cm}^{-1}$) carboxylate vibrations, $\Delta\nu = 164 \text{ cm}^{-1}$, is smaller than that observed with the corresponding acid ($\Delta\nu_i \approx 270 \text{ cm}^{-1}$) in agreement with the monodentate coordination mode of the carboxylate groups [56]. The presence of broad $\nu_{\text{N-H}}$ bands in the range $3223\text{--}3254 \text{ cm}^{-1}$ is related to the cysteate NH moieties bonded to the metal ions, and the large band observed at 3430 cm^{-1} is assigned to the coordinated water molecule (Fig. S1). For compound **2**, strong absorption bands at

2040 cm^{-1} and 1299.9 cm^{-1} in the IR spectra correspond to $\nu_{\text{as}}(\text{N}_3)$ and $\nu_{\text{s}}(\text{N}_3)$, and some characteristic bands for 2,2'-dmbpy in the region of 1041, 1612, 1550.7, 1685.7, 1446, 914 and 833 cm^{-1} (Fig. S2). The compound **3**, show some characteristic bands for 2,2'-dmbpy in the region: 1041.6, 1558, 1620, 1444, 931 and 831 cm^{-1} . The large band observed in the region: $3200\text{--}3500 \text{ cm}^{-1}$ corresponds to the solvation water molecules (Fig. S3).

3.5. Thermogravimetric analysis

The thermal stability of the compounds was evaluated by thermogravimetric analysis between ambient temperature and $600 \text{ }^\circ\text{C}$ in air ($5 \text{ }^\circ\text{C min}^{-1}$) for compound **1** and ambient temperature and $1000 \text{ }^\circ\text{C}$ for compound **3**.

The TGA of compound **1** (see trace in Fig. 8) revealed that the decomposition takes place in three steps. The first is observed at $150 \text{ }^\circ\text{C}$ (-5%) and indicates the loss of the coordinated water molecule. The second loss is observed at $250 \text{ }^\circ\text{C}$ (-13.78%) and indicates the decomposition of the (COO⁻) and (NH₂) groups. Then, the very exothermic final weight loss of 58% starting at $430 \text{ }^\circ\text{C}$, is associated to the decomposition of the dmbpy (C₁₂N₂H₁₂) and (C₂H₃SO₃⁻) into CuO.

The TGA trace of compound **3** is shown in Fig. 9; a first weight loss is observed between $60\text{--}120 \text{ }^\circ\text{C}$ (-15%) and corresponds to the removal of the seven solvation water molecules ($-7\text{H}_2\text{O}$) and the chlorine anion (Cl⁻). The second loss observed around $190 \text{ }^\circ\text{C}$ (-20%) corresponds to the tetrachlorocobaltate anion [CoCl₄]²⁻, while the third

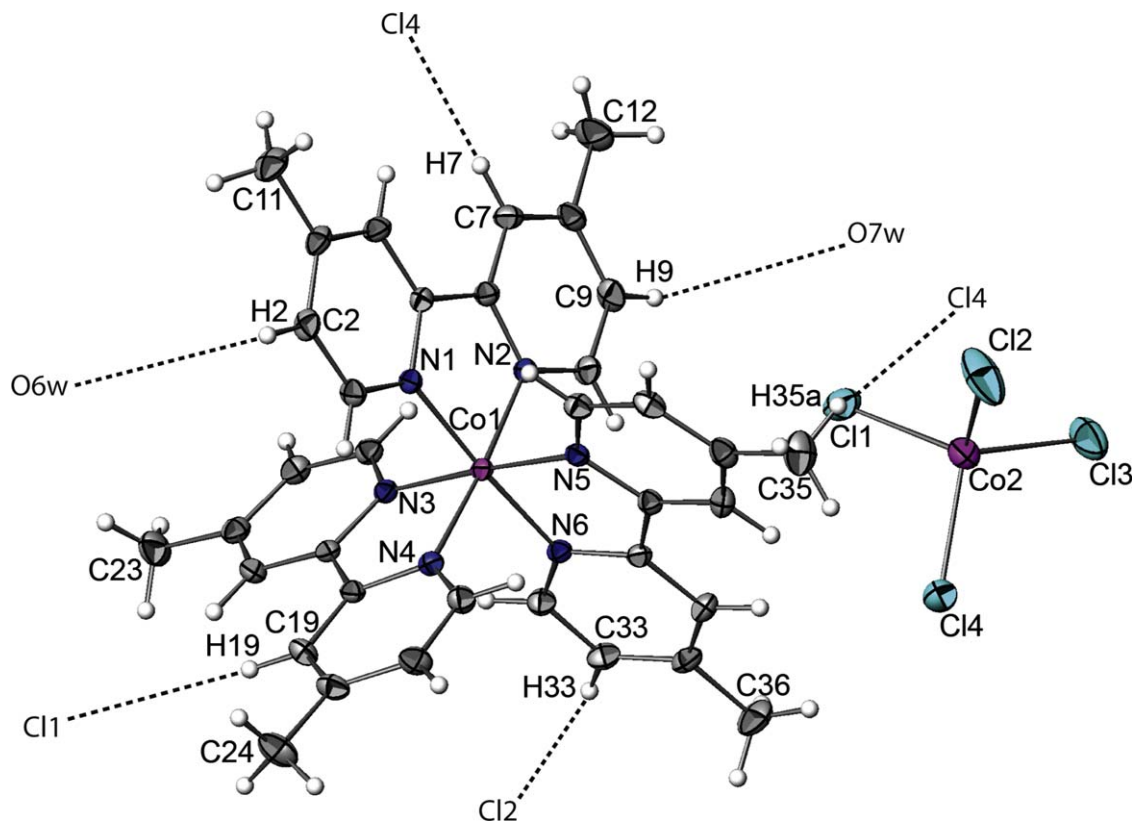


Fig. 6. ORTEP view (ATOMS software) of **3** ($[\text{Co}^{\text{II}}(\text{dmbpy})_3][\text{Co}^{\text{II}}\text{Cl}_4]\cdot\text{Cl}\cdot 7\text{H}_2\text{O}$) with partial labeling scheme. The ellipsoids enclose 30% of the electronic density. Dashed lines indicate inter molecular H-bonds. Selected distances (Å) and angles ($^\circ$): Co1-N1 = 1.937(3), Co1-N2 = 1.947(3), Co1-N3 = 1.930(3), Co1-N4 = 1.936(3), Co1-N5 = 1.925(3), Co1-N6 = 1.925(3), Co2-Cl1 = 2.2982(16), Co2-Cl2 = 2.267(2), Co2-Cl3 = 2.2790(17), Co2-Cl4 = 2.258(2), N1-Co1-N2 = 83.20(10), N1-Co1-N4 = 93.59(11), N1-Co1-N6 = 176.20(11), N2-Co1-N4 = 175.98(11), N2-Co1-N5 = 89.23(10), Cl3-Co2-Cl4 = 109.85(6), Cl1-Co2-Cl4 = 110.04(7), Cl1-Co2-Cl2 = 113.69(6), Cl2-Co2-Cl3 = 110.20(6), Cl2-Co2-Cl4 = 106.54(6).

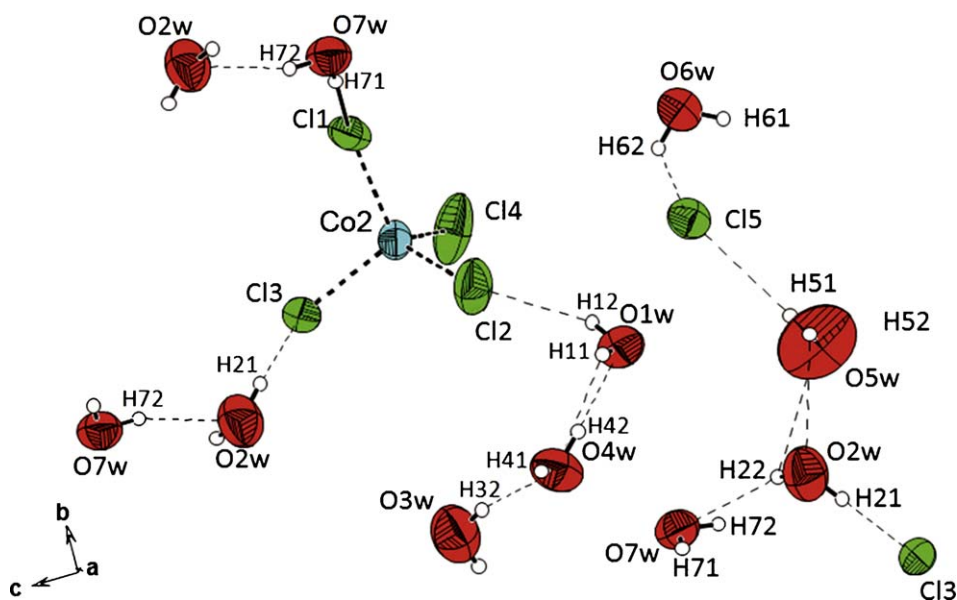


Fig. 7. Partial view of anion $[\text{CoCl}_4]^{2-}$ in complex **3** showing the hydrogen bonds in dashed lines.

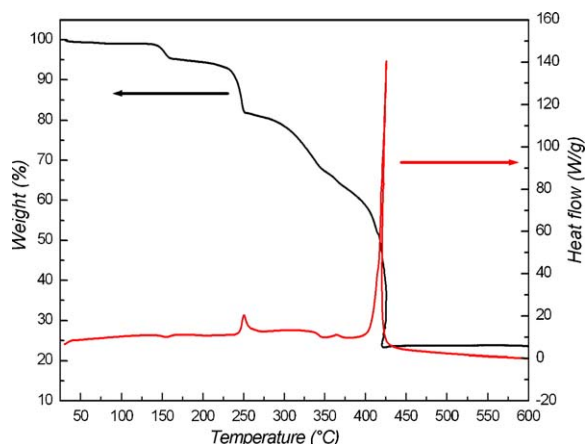


Fig. 8. TGA and TDA curves of **1**.

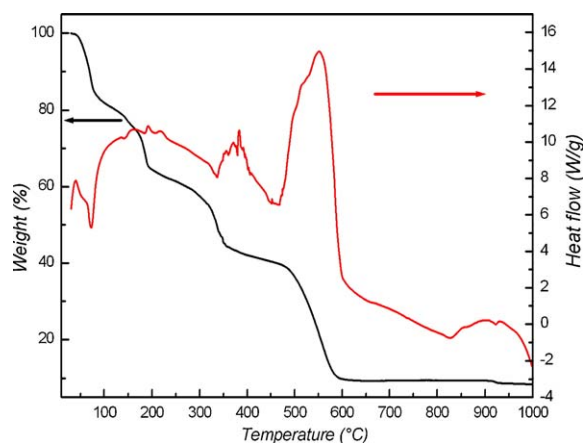


Fig. 9. TGA and TDA curves of **3**.

loss is observed at 350 °C (–20%) which corresponds to the decomposition of one molecule of dmbpy ($C_{12}N_2H_{12}$). It is worth noting that this decomposition occurs at quite high temperature and that the combustion of the two other molecules of (dmbpy) is very exothermic, leading to an overflow of the temperature regulation. The final total weight loss of 35% at 550 °C corresponds well to the decomposition total of Complex into Co_3O_4 .

For compound **2** the measure has not been realized because it contains the “explosive” azide group (N_3).

4. Conclusion

Three new coordination complexes $[Cu(Cyst)(dmbpy)(H_2O)]$ (**1**), $[Mn(dmbpy)_2(N_3)(Cl)]$ (**2**) and $H_2O.Cl[Co(dmbpy)_3].[CoCl_4]$ (**3**) based on mixed ligand with different structure motifs are synthesized and structurally characterized. The complexes **1** and **2** are mononuclear, while the complex **3** is dinuclear. The molecular structure of complex **1** consists in copper metal center in pyramidal square base chelated to one L-cyst acid and one dmbpy and one water molecule in apical position. The complex **2** is hexa coordinated by two dmbpy, one azide and Cl^- anions. The complex **3** is composed of $[Co^{II}(dmbpy)_3]$ cation,

$[Co^{II}Cl_4]$ anion, Cl^- and seven water molecules. Thermal decomposition of complex **1** and **3** reveals that the Cu complex decomposes in three steps whereas the Co complex decomposes in four steps and transforms into the corresponding metal oxide.

Future studies will focus on the construction of new metal–organic coordination polymers from the cysteic acid and other co-ligands for the design of new chiral magnetic systems. This approach is very promising to investigate the complicated issue of the coupling between magnetism and chirality.

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Appendix A. Supplementary data

Crystallographic data for **1–3** (excluding structure factors) have been deposited in the Cambridge Crystallographic Data Centre as Supplementary publication No. CCDC 724925, 724926 and 777592. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.crci.2010.12.002](https://doi.org/10.1016/j.crci.2010.12.002).

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