

Crystal Structures and Stability of Two Bipyridyl Complexes of Metal Chloroacetates

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The complexes $\text{Mn}(\text{Cl}_3\text{CCOO})_2(4,4'\text{-bpy})$ (**1**) and $[\text{Cu}_2(\text{ClCH}_2\text{COO})(2,2'\text{-bpy})_2(\text{OH})(\text{H}_2\text{O})](\text{NO}_3)_2$ (**2**) (bpy = bipyridine) were generated under mild reaction conditions and characterized by IR spectra, thermogravimetric analysis (TGA), X-ray powder diffraction (XRD), and single crystal X-ray diffraction. Compound **1** exhibits a two-dimensional network with octahedrally coordinated Mn(II) atoms linked by 4,4'-bpy ligands and Cl_3CCOO^- ligands. Compound **2** features a supramolecular structure of binuclear complexes, with edge-sharing five-coordinated square-pyramidal units bridged by the $\text{ClCH}_2\text{COO}^-$ ligand, an OH^- group and a water molecule. Complex **1** crystallizes in the orthorhombic space group *Pbcn* with cell parameters: $a = 16.5390(17)$, $b = 11.6396(17)$, $c = 9.9181(12)$ Å, $V = 1909.3(4)$ Å³, $Z = 4$, $wR2 = 0.1576$. Complex **2** crystallizes in the triclinic space group *P1* with cell parameters: $a = 7.6190(15)$, $b = 11.151(2)$, $c = 16.640(3)$ Å, $\alpha = 73.13(3)$, $\beta = 80.89(3)$, $\gamma = 74.51(3)^\circ$, $V = 1298.73(4)$ Å³, $Z = 2$, $wR2 = 0.1265$.

Key words: Crystal Structures, Metal Chloroacetate Complexes, Thermal Behavior

Introduction

Transition metal carboxylate complexes have received extensive attention due to the wide application and various structural features of these compounds [1–3]. Besides biological chemistry [4] and catalysis [5–8], the study of exchange-coupling interactions between adjacent metal ions is of major interest in the field of magnetochemistry [9–12]. Ligands such as 2,2'-bipyridine (2,2'-bpy), 1,10-phenanthroline (phen) and 4,4'-bipyridine (4,4'-bpy) have been widely used as substitutes for amino acid side groups in biomimetic chemistry and as rigid ligands for the construction of organometallic supramolecular complexes. The coordination chemistry of chloroacetic or trichloroacetic acid has also received a great deal of attention [13–19]. However, there are few structurally characterized metal chloroacetates with aromatic nitrogen-donor ligands [20]. Based on the above consideration, in this contribution we wish to report two ternary complexes, $\text{Mn}(\text{Cl}_3\text{CCOO})_2(4,4'\text{-bpy})$ (**1**) and $[\text{Cu}_2(\text{ClCH}_2\text{COO})(2,2'\text{-bpy})_2(\text{OH})(\text{H}_2\text{O})](\text{NO}_3)_2$ (**2**) (bpy = bipyridine). Compound **1** exhibits a 2D polymeric network with octahedrally coor-

dinated Mn(II) atoms linked by 4,4'-bpy and Cl_3CCOO^- ligands; compound **2** features a supramolecular structure with dinuclear units featuring edge-sharing five-coordinated square-pyramidal entities with $\mu_2\text{-ClCH}_2\text{COO}^-$, $\mu_2\text{-OH}^-$ groups and $\mu_2\text{-H}_2\text{O}$ bridges.

Experimental Section

Measurements of physical properties

All chemicals were reagent grade and were used without further purification. Elemental analysis was performed using a Perkin-Elmer 2400 CHNS/O analyzer. The infrared spectrum of KBr pellets in the range 4000–400 cm^{-1} was recorded using a Nicolet AVATAR-370 spectrophotometer. The combined thermogravimetric and differential thermal analysis (TG/DSC) was carried out in the range 25–600 °C on powdered samples using an STA 409 PC analyzer with a heating rate of 10 °C min^{-1} . X-Ray powder diffraction was performed using an X'Pert PRO DY2198 diffractometer.

Preparation of $\text{Mn}(\text{Cl}_3\text{CCOO})_2(4,4'\text{-bpy})$ (**1**)

MnCO_3 (0.12 g, 1.0 mmol) and Cl_3CCOOH (0.33 g, 2.0 mmol) were dissolved in a water-ethanol mixture (1 : 1 v/v; 20 mL). The mixture was stirred for 15 min at 60 °C

Table 1. Crystal data and structure refinement for **1** and **2**.

Formula	C ₁₄ H ₈ Cl ₆ MnN ₂ O ₄	C ₂₂ H ₂₁ ClCu ₂ N ₆ O ₁₀
<i>Mr</i>	535.86	691.98
Crystal size, mm ³	0.4 × 0.36 × 0.30	0.42 × 0.40 × 0.32
Crystal system	orthorhombic	triclinic
Space group	<i>Pbcn</i>	<i>P</i>
<i>a</i> , Å	16.5390(17)	7.6190(15)
<i>b</i> , Å	11.6396(17)	11.151(2)
<i>c</i> , Å	9.9181(12)	16.640(3)
α , deg	90	73.13(3)
β , deg	90	80.89(3)
γ , deg	90	74.51(3)
<i>V</i> , Å ³	1909.3(4)	1298.73(4)
<i>Z</i>	4	2
<i>d</i> _{calcd.} , g/cm ^{−3}	1.864	1.77
μ (MoK α), cm ^{−1}	1.555	1.809
<i>F</i> (000), e	1060	700
<i>hkl</i> range	−21 ≤ <i>h</i> ≤ 21 −15 ≤ <i>k</i> ≤ 13 −12 ≤ <i>l</i> ≤ 13	−9 ≤ <i>h</i> ≤ 9 −14 ≤ <i>k</i> ≤ 14 −21 ≤ <i>l</i> ≤ 21
$((\sin \theta)/\lambda)_{\max}$, Å ^{−1}	0.2829	0.0284
Refl. measured	16828	12691
Refl. unique	2230	5864
<i>R</i> _{int}	0.07625	0.021
Param. refined	126	370
<i>R</i> 1(<i>F</i>)/ <i>wR</i> 2(<i>F</i> ²) ^a	0.078/0.186	0.057/0.137
(all reflexions)		
<i>A</i> , <i>B</i> values for weighting scheme ^b	0, 0	0.07, 1.8898
GoF(<i>F</i> ²) ^c	0.836	1.083
$\Delta\rho_{\text{fin}}$ (max/min), e Å ^{−3}	0.87/−0.94	1.07/−0.77

^a $R(F) = \Sigma ||F_o| - |F_c|| / \Sigma |F_c|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_c^2)^2]^{1/2}$;

^b $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, with $P = (F_o^2 + 2F_c^2)/3$;

^c $\text{GoF}(F^2) = S = \{\Sigma [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$, where *n* is the number of reflexions and *p* is the total number of parameters refined.

and then 4,4'-bpy (0.16 g, 1.0 mmol) was added. The mixture was further stirred for another 1 h at 60 °C, then filtered, and the resultant filtrate left to stand for slow evaporation at r.t. Colorless single crystals of **1** were obtained after a period of 30 d (yield 85% based on the initial MnCO₃ input). C₁₄H₈Cl₆MnN₂O₄ (535.86): calcd. C 31.38, H 1.50, N 5.23; found C 31.41, H 1.51, N 5.19. – IR: ν = 3063m, 3007m, 1965w, 1719s, 1667vs, 1602s, 1530m, 1487m, 1418m, 1354vs, 1221m, 1100w, 1072m, 1043m, 1003m, 942w, 828vs, 726s, 681vs, 629m, 570m, 534m, 467w, 431w cm^{−1}.

Preparation of [Cu₂(ClCH₂COO)(2,2'-bpy)₂(OH)(H₂O)](NO₃)₂ (**2**)

Cu(NO₃)₂ · 3H₂O (0.24 g, 1.0 mmol) and ClCH₂COOH (0.33 g, 2.0 mmol) were dissolved in a water-ethanol mixture (1:1 v/v; 40 mL). The mixture was stirred for 5 min at r.t. and then 2,2'-bpy (0.16 g, 1.0 mmol) was added. The mixture was further stirred for another 1 h at 60 °C, then filtered, and the resultant filtrate left to stand for

Table 2. Selected interatomic distances (Å) and bond angles (deg) for **1**.

Mn1–O1	2.144(3)	Mn1–N1	2.276(4)
Mn1–O1 ^{#1}	2.144(3)	Mn1–N2 ^{#4}	2.277(3)
Mn1–O2 ^{#2}	2.186(2)	Mn1 ^{#5} –N2	2.277(3)
Mn1–O2 ^{#3}	2.186(2)	C7–O1	1.236(4)
Mn1 ^{#3} –O2	2.186(2)	C7–O2	1.230(4)
O1–Mn1–O1 ^{#1}	179.5(1)	O2 ^{#3} –Mn1–N1	85.48(6)
O1–Mn1–O2 ^{#2}	87.26(1)	O2 ^{#3} –Mn1–N2 ^{#4}	94.52(6)
O1–Mn1–O2 ^{#3}	92.78(1)	O1–C7–C8	114.3(3)
O1–Mn1–N1	90.24(6)	O2–C7–O1	130.0(3)
O1–Mn1–N2 ^{#4}	89.76(6)	O2–C7–C8	115.7(3)
O1 ^{#1} –Mn1–O2 ^{#2}	92.78(1)	C7–O1–Mn1	146.2(2)
O1 ^{#1} –Mn1–O2 ^{#3}	87.26(1)	C7–O2–Mn1 ^{#3}	144.0(2)
O1 ^{#1} –Mn1–N1	90.24(6)	C6–N2–C6 ^{#1}	117.2(4)
O1 ^{#1} –Mn1–N2 ^{#4}	89.76(6)	C6–N2–Mn1 ^{#5}	121.4(2)
O2 ^{#2} –Mn1–O2 ^{#3}	171.0(1)	C6 ^{#1} –N2–Mn1 ^{#5}	121.4(2)
O2 ^{#2} –Mn1–N1	85.48(6)	N1–Mn1–N2 ^{#4}	180
O2 ^{#2} –Mn1–N2 ^{#4}	94.52(6)		

Symmetry transformations used to generate equivalent atoms: ^{#1} 1 − *x*, *y*, 1/2 − *z*; ^{#2} *x*, 1 − *y*, *z* + 1/2; ^{#3} 1 − *x*, 1 − *y*, −*z*; ^{#4} *x*, *y* − 1, *z*; ^{#5} *x*, 1 + *y*, *z*.

slow evaporation at r.t. Blue single crystals of complex **2** were obtained after a period of 40 d (yield 90% based on initial Cu(NO₃)₂ · 3 H₂O input). C₂₂H₂₁ClCu₂N₆O₁₀ (691.98): calcd. C 38.19, H 3.06, N 12.14; found C 38.22, H 3.08, N 12.12. – IR: ν = 3494m, 3415m, 3107m, 3063m, 1597s, 1497m, 1441m, 1383vs, 1315m, 1261m, 1164m, 1107m, 1025m, 775m, 732m, 695m, 661m, 497m, 461m cm^{−1}.

X-Ray structural analyses

Diffraction experiments were carried out at r.t. on a Bruker Smart CCD diffractometer with graphite-monochromated MoK α radiation (λ = 0.71073 Å) for cell determination and subsequent data collection. SHELXS/L-97 programs [21,22] were used for structure solution and refinement. The structure of complex **1** was solved by Direct Methods, while that of **2** was solved by Patterson Methods. The hydrogen atoms associated with carbon atoms were generated geometrically, whereas the H₂O and OH[−] hydrogen atoms were located from the difference Fourier syntheses. All non-hydrogen atoms were finally refined with anisotropic displacement parameters by full-matrix least-squares techniques, and hydrogen atoms with isotropic displacement parameters. The relevant crystal and refinement data and the experimental conditions are summarized in Table 1. Selected interatomic distances and bond angles are given in Tables 2 and 3.

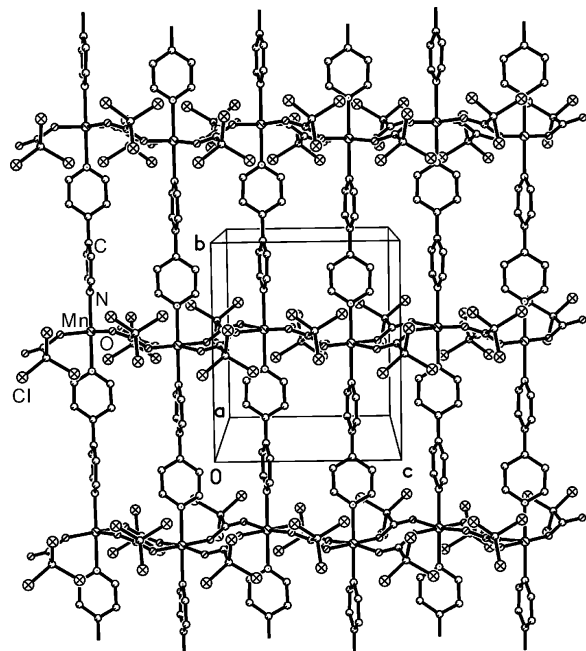
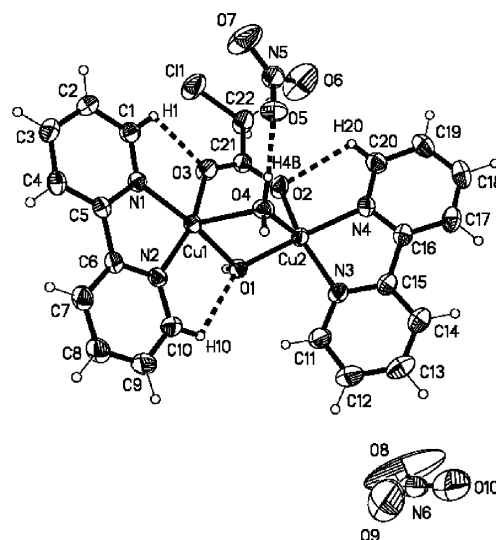
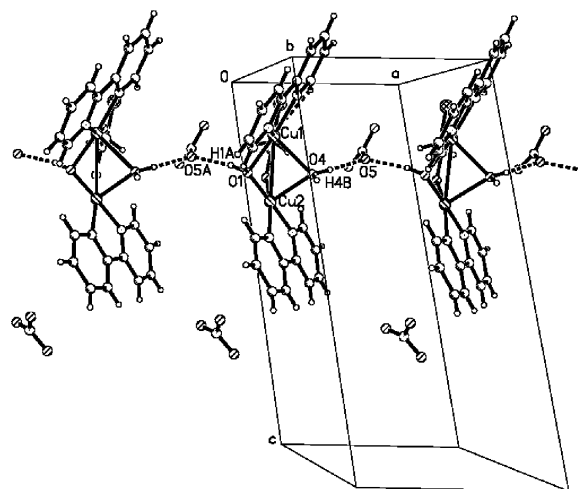
CCDC 649429 (**1**) and 649430 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallo-

Table 3. Selected interatomic distances (Å) and bond angles (deg) for **2**.

Cu1–O1	1.932(3)	Cu2–O2	1.944(3)
Cu1–O3	1.965(3)	Cu2–O4	2.427(3)
Cu1–O4	2.318(3)	Cu2–N3	2.000(3)
Cu1–N1	1.992(3)	Cu2–N4	2.003(3)
Cu1–N2	2.000(3)	O2–C8	1.249(4)
Cu2–O1	1.918(3)	O3–C8	1.248(4)
O1–Cu1–O3	95.48(1)	O2–Cu2–N3	162.1(1)
O1–Cu1–O4	80.81(1)	O2–Cu2–N4	88.40(1)
O1–Cu1–N1	94.66(1)	O3–Cu1–O4	94.08(1)
O1–Cu1–N2	173.1(1)	O3–Cu1–N1	163.5(1)
O1–Cu2–O2	93.26(1)	N1–Cu1–O4	100.4(1)
O1–Cu2–O4	78.26(1)	N2–Cu1–O4	105.1(1)
O1–Cu2–N3	96.95(1)	Cu1–O4–Cu2	79.90(1)
O1–Cu2–N4	177.7(1)	Cu2–O1–Cu1	104.7(1)
O2–Cu2–O4	101.6(1)		

Hydrogen bonds

D–H...A	D–H	H...A	D...A	D–H...
O1–H1A...O5 ^{#1}	0.90	2.01	2.896(4)	170.3
O4–H4A...O9 ^{#2}	0.90	2.17	2.967(1)	147.5
O4–H4A...O10 ^{#2}	0.90	2.46	3.266(1)	150.6
O4–H4B...O5	0.90	1.80	2.699(4)	175.5
C1–H1...O3	0.93	2.37	2.872(4)	113.4
C10–H10...O1	0.93	2.54	3.050(5)	115.0
C20–H20...O2	0.93	2.39	2.883(5)	113.0

Symmetry codes: ^{#1} $x-1, y, z$; ^{#2} $-x, 1-y, 1-z$.Fig. 1. The octahedrally coordinated Mn(II) atoms linked by 4,4'-bpy and carboxylate ligands into 2D sheets in the crystal structure of **1**.graphic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.Fig. 2. ORTEP view of the molecular structure of **2** and atom labelling scheme (displacement ellipsoids drawn at 40 % probability).Fig. 3. 1D supramolecular chain along the [100] direction linked by O–H...O hydrogen bonds in the crystal structure of **2**.

Results and Discussion

IR spectra

The infrared spectrum of compound **1** shows the aromatic $\nu(\text{C-H})$ stretching vibration peaks at 3063 and 3007 cm^{-1} . The absorption at 1602 cm^{-1} should be assigned to $\nu_{\text{as}}(\text{CO}_2^-)$, and the absorption peaks centered at 1378 and 1354 cm^{-1} to $\nu_{\text{s}}(\text{CO}_2^-)$ stretching vibrations. The 4,4'-bpy-based absorption peaks reside at 1530, 828, 726, 681 cm^{-1} .

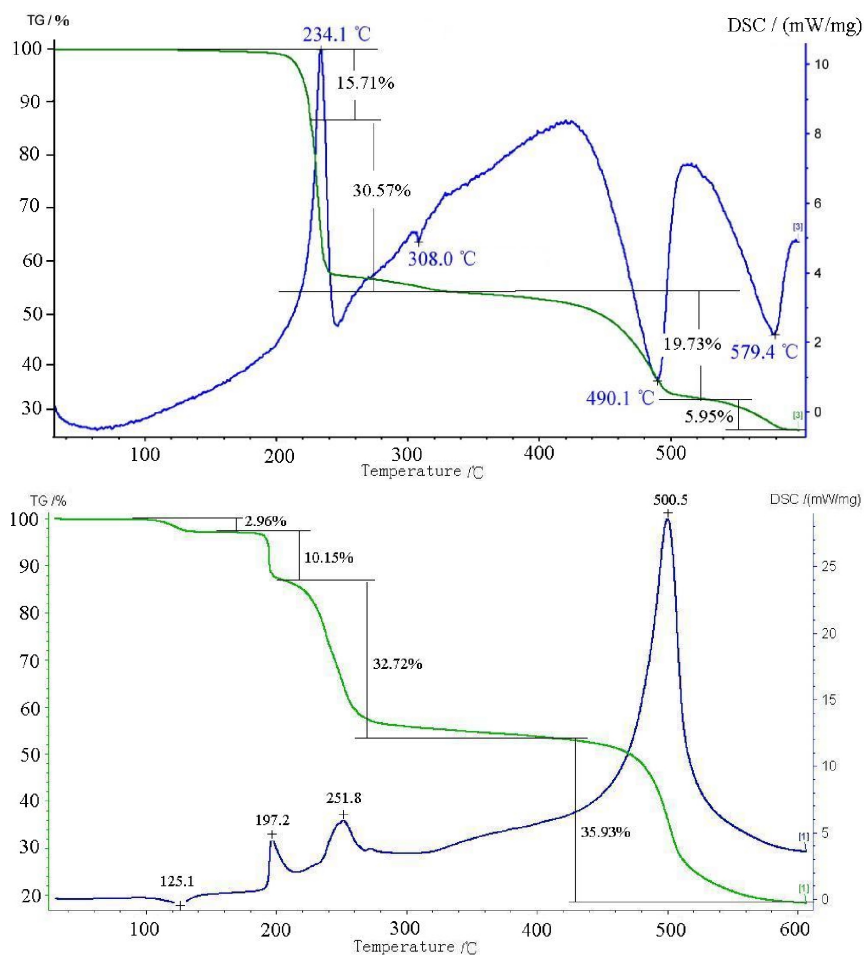


Fig. 4. Thermogravimetric analysis (TGA) diagrams for compounds **1** (top) and **2** (bottom).

The infrared spectrum of compound **2** shows $\nu(\text{O-H})$ vibrations of a coordinated water molecule and an OH^- group at 3494 and 3415 cm^{-1} , and the aromatic $\nu(\text{=C-H})$ stretching vibration peaks at 3107 and 3063 cm^{-1} . The absorption at 1597 cm^{-1} should be assigned to $\nu_{\text{as}}(\text{CO}_2^-)$ and the strong absorption peak at 1383 cm^{-1} to $\nu_{\text{s}}(\text{NO}_3^-)$ stretching vibrations. The 2,2'-bpy-based absorption peaks reside at 836 , 775 , 732 , and 695 cm^{-1} .

Compared with the bands of carboxylic acid molecules, the $\nu_{\text{as}}(\text{CO}_2^-)$ stretching vibration peaks of **1** and **2** are significantly blue-shifted indicating the coordination interactions.

Structure descriptions

$\text{Mn}(\text{Cl}_3\text{CCOO})_2(4,4'\text{-bpy})$ (**1**)

Complex **1** crystallizes in the orthorhombic space group *Pbcn* and features a two-dimensional metal-

organic framework with the Mn(II) atoms bridged by trichloroacetate and 4,4'-bipyridine ligands (Fig. 1). The six-coordinated Mn atom is surrounded by two nitrogen atoms of two 4,4'-bpy ligands and four oxygen atoms of four carboxylate ligands in a distorted octahedral geometry. The trichloroacetate ligands act as bridges linking the Mn atoms to form zigzag chains along the [001] direction, which are further interlinked by 4,4'-bpy ligands into 2D sheets parallel to (101). The 2D framework displays (4,4) topology with the Schläfli symbol $4^4.6^2$ and the vertex symbol or long symbol of $4.4.4.4.6_2.6_2$ [23–25].

The Mn–O mean distance ($2.165(3)\text{ \AA}$) is shorter than the Mn–N mean distance ($2.277(4)\text{ \AA}$). The *cis* bond angles at the central Mn atom fall in the range of $85.5\text{--}94.5^\circ$, and the *trans* bond angle $\angle \text{O}2^{\#2}\text{--Mn1--O}2^{\#3}$ is 171.0° (Table 2), suggesting a significant deviation from a perfect octahedral coordination.

$[Cu_2(ClCH_2COO)(2,2'-bpy)_2(OH)(H_2O)](NO_3)_2$ (**2**)

Complex **2** crystallizes in the triclinic space group $P\bar{1}$, with binuclear $[Cu_2(\mu_2-ClCH_2COO)(2,2'-bpy)_2-(\mu_2-OH)(\mu_2-H_2O)]^{2+}$ complex cations and nitrate anions. Each of the binuclear cations consists of two edge-sharing distorted square-pyramidally coordinated units, featuring one chloroacetate anionic ligand, one water molecule, one hydroxyl anion, and two 2,2'-bpy molecules as ligands for Cu(II). The chloroacetate ligand adopts a bidentately bridging *syn-syn* coordination mode, with oxygen atoms linking two Cu(II) atoms; both the water molecule and the hydroxyl group also act as μ_2 -bridges (Fig. 2). The coordinated water molecule resides on the capping positions of the two square-pyramids, with the bond lengths Cu1–O4 = 2.32(4) and Cu2–O4 = 2.43(4) Å being longer than the other Cu–O and Cu–N bond lengths (Table 3), which may be due to the Jahn-Teller elongation effect [26].

Hydrogen bonds stabilize the structure. The hydroxyl group and the carboxylate oxygen atoms accept hydrogen atoms from 2,2'-bpy ligands to generate intramolecular interactions (Fig. 2). Along the [100] direction, the complex molecules are interlinked by intermolecular O–H...O hydrogen bonds into chains, *via* the coordinated water molecule and the hydroxyl group which donate hydrogen atoms (H4B and H1A) to nitrate oxygen atoms (Fig. 3). The chains are held together by π - π interactions to form 2D sheets parallel to (021). The resultant sheets are further stabilized by intermolecular hydrogen bonding interactions into a 3D supramolecular network, where the coordinated water molecules contribute hydrogen atoms (H4A) to nitrate oxygen atoms (O9 and O10) (Table 3).

Thermal behavior

The DSC curve of **1** exhibits one exothermic peak centered at 234 °C and three endothermic ones at 308, 490, and 579 °C. Thermogravimetric analysis (TGA) (Fig. 4) reveals that **1** possesses high thermal stability. There is no weight loss from r.t. to 200 °C. The observed weight loss of 46.3 % at 400 °C is in good agreement with the calculated value of 47.0 % for release of one mole of 4,4'-bpy and two moles of CO₂ per formula unit. Upon further heating over the temperature range 400–600 °C, the TG curve indicates a weight loss of 25.7 %,

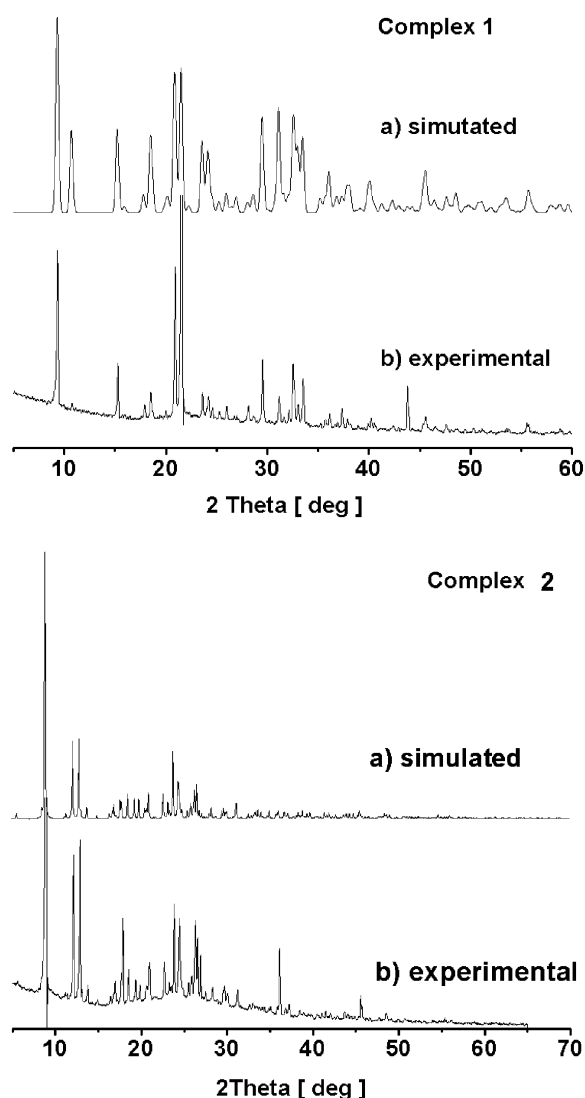


Fig. 5. Experimental and simulated XRD patterns for compounds **1** and **2**.

which agrees well with the calculated value of 26.5 % for release of two moles of Cl₂ per formula unit. The residue of 28.2 % at 600 °C is MnCl₂·2 H₂O (calcd. 28.0 %).

The DSC curve of **2** shows one exothermic peak centered at 125 °C and three endothermic peaks centered at 197, 251 and 200 °C (Fig. 4). The observed weight loss of 3.0 % at 140 °C is close to the calculated value of 2.6 % for release of one H₂O per formula unit. Over 180–210 °C, weight loss of 10.2 % corresponds well to the calculated value of 11.3 % for release of one 2,2'-bpy ligand per two formula units. Upon heat-

ing up to 300 °C, the sample loses weight of 32.7 %, which is close to the calculated value of 33.8 % for the release of the other 2,2'-bpy ligand. After experiencing a plateau, upon further heating over the temperature range 400–600 °C, the TG curve indicates an additional weight loss of 35.9 % in accordance with leaving a residue of 18.3 % at 600 °C identified as Cu powder (calcd. 18.4 %).

XRD patterns of **1** and **2**

X-Ray powder diffraction (XRD) data of complexes **1** and **2** were collected with CuK α radiation ($\lambda = 1.5418$ Å). Both experimental XRD patterns agreed well with the simulated ones generated on the basis of the single crystal analyses for the title compounds, suggesting the phase purity of the products. The differences in intensity may be due to the preferred orientation of the powder samples (Fig. 5).

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