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Synthesis and Characterization of New Anderson-Type Polyoxometalates: $[M((1,10\text{-phen})(OH)_x]_3[Cr(OH)_6Mo_6O_{18}]\cdot 16H_2O$ (M=Cr, Mn, Co, Ni, Cu; x=1,2)

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Abstract: Five new Anderson-type polyoxometalate compounds $[M((1,10\text{-phen})(OH)_x]_3[Cr(OH)_6Mo_6O_{18}]\cdot 16H_2O$ (M=Cr(**1**), Mn(**2**), Co(**3**), Ni(**4**), Cu(**5**); x=1,2) were obtained from $Na_2MoO_4{\cdot}2H_2O$ and $CrCl_3{\cdot}6H_2O$ within acidic aqueous medium (pH=2-3). The compounds are characterized by means of FT-IR, TGA, ICP-MS, and elemental analysis techniques. The structural analysis show that compounds (**1-5**) consist of a Anderson-type polyanion $[Cr(OH)_6Mo_6O_{18}]^{3-}$.

Keywords: Molybdenum, Chromium, Polyoxometalate, Anderson-Evans.

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1. INTRODUCTION

Polyoxometalates (POMs) as a family of metal-oxo clusters have attracted extensive attention due to their various structural characteristics, highly negative charges, excellent redox ability, and potential applications in catalysis, medicine, materials science, protein crystallography, nanotechnology and photochemistry (1-12). POMs are classified different categories such as Anderson, Lindqvist, Keggin, Waugh, Dawson, and Silverton. The Anderson-type heteropolyanions with the general formula $[Hy(XO_6)M_6O_{18}]^{n-}$ (X: Co, Ni, Cr or Mn and M=Mo(VI) or W(VI)) are an essential subfamily of POMs and have been of great importance due to their attractive magnetic and electronic properties. These POMs are ideal inorganic building blocks for creating hybrid materials since their easily get at covalent modification (13). In addition, chromium-containing POMs have interesting physicochemical properties (14). In recent years, interest in chromium derivatives of Anderson-type POMs have been increasing (15-17). $[(Gly)_2Cu][Na(H_2O)_4Cr(OH)_6Mo_6O_{18}]\cdot 9.5H_2O$ (Gly=glycine), has been synthesized and structurally characterized by An and co-workers (18). The luminescent properties of $(NH_4)_3[Cr(OH)_6Mo_6O_{18}]\cdot nH_2O$ have been investigated for the first time (19). $[Cr(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)_2\}_2]$ $[Cr(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)Cl\}_2](H_2O)\cdot 5H_2O$ has been reported by Shivaiah and Das (20). Shi and co-workers have been successfully synthesized compounds based on the $[Cr(OH)_6Mo_6O_{18}]^{3-}$ and lanthanide ions (21-22). $[Cu(phen)]_2[CrMo_6H_5O_{24}]$ has been hydrothermally synthesized (23). $(H_3O)[(3\text{-}C_5H_7N_2)_2(Cr(OH)_6Mo_6O_{18})]\cdot 3H_2O$ was also hydrothermally synthesized and showed high catalytic activity for oxidation of acetone (24). $Na_4[Ni(OH)_6Mo_6O_{18}]\cdot 16H_2O$ has been reported by Gumerova and co-workers (25). Liu and co-workers have reported chromium-centered Anderson-Evans type polytungstate $Na_6[H_3Cr^{III}W_6O_{24}]\cdot 22H_2O$ (14). Tewari and co-workers have synthesized a series of Anderson-type clusters coordinated with lanthanides $[Ln(H_2O)_7\{Cr(OH)_6Mo_6O_{18}\}]\cdot 4H_2O$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) (26). $(NH_4)_3[CrMo_6O_{18}(OH)_6]$ have been efficient in the direct oxidation of a variety of alcohols (27).

In the current work, the new chromium-containing Anderson-type POM compounds $[M((1,10\text{-phen})(OH)_x]_3[Cr(OH)_6Mo_6O_{18}]\cdot 16H_2O$ (M=Cr(**1**), Mn(**2**), Co(**3**), Ni(**4**), Cu(**5**); x=1,2) have been synthesized and characterized by FT-IR, TGA, ICP-MS, and elemental analysis.

2. MATERIAL AND METHOD

2.1. General Methods

All reagents were purchased from commercial sources and used as received. FT-IR spectrum was recorded in 400–4000 cm^{-1} with a Perkin Elmer LR 64912 C spectrometer using KBr pellets. Elemental analyses (i.e., for C, H, and N) were performed on a LECO-932 CHNS model analyzer. ICP-MS analyses were performed on ICP-MS Agilent Technologie 7700. TGA analysis was carried out on Hitachi Exstar TG/DTA 7300.

2.2. Synthesis of Compounds

A mixture of $Na_2MoO_4{\cdot}2H_2O$ (157 mg, 0.65 mmol) and $CrCl_3{\cdot}6H_2O$ (69 mg, 025 mmol) was dissolved in distilled water (5 mL). Glacial acetic acid (1 mL) was then added to the mixture with by stirring at room temperature for about 30 min. Afterward, 1,10-phenanthroline monohydrate (155 mg, 0.78 mmol) and metal chloride salts (0.78 mmol) ($CrCl_3{\cdot}6H_2O$, $MnCl_2{\cdot}4H_2O$, $CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$) dissolved in a mixture of water (2 mL) were added to the resulting reaction mixture, stirred for 2 hours. The product was filtered off, washed with water, and dried under a vacuum at 50 °C.

$[Cr(1,10\text{-phen})(OH)_2]_3[Cr(OH)_6Mo_6O_{18}]16H_2O$ (1):

Yield: 122 mg, 22%. FT-IR (KBr pellets): υ= 3067 (w), 1623 (s), 1597 (s), 1544 (s), 1519 (m), 1469 (m), 1451 (m), 1427 (s), 1338 (m), 1316 (m), 1225 (s), 1146 (s), 1107 (m), 1036 (m), 936 (m), 911 (m), 846 (m), 774 (m), 717 (m), 649 (m), 496 (m), 463 (m), 426 (m), 410 (m) cm^{-1}. Elem. Anal. Calcd. $Cr_4Mo_6C_{36}H_{68}N_6O_{46}$ (2104.56 g/mol): C, 20.55, H, 3.26, N, 3.99, Mo, 27.35, Cr, 9,88. found: C, 20.59, H, 3.11, N, 4.09, Mo, 29.35 (ICP-MS), Cr, 9.77 (ICP-MS). TGA (loss of $16H_2O$): calcd. 13.69%, found 13.16%; (loss of $[Cr(1,10\text{-phen})(OH)_2]_3$): calcd. 37.95%, found 38.07%.

$[Mn(1,10\text{-phen})(OH)]_3[Cr(OH)_6Mo_6O_{18}]{\cdot}16H_2O$ (2):

Yield: 118 mg, 22%. FT-IR (KBr pellets): υ= 3369 (w), 1623 (s), 1585 (s), 1579 (m), 1517 (s), 1425 (s), 1342 (s), 1224 (s), 1144 (s), 1103 (s), 941 (m), 913 (m), 888 (m), 849 (m), 781 (m), 724 (m), 648 (m), 496 (m), 421 (m) cm^{-1}. Elem. Anal. Calcd. $CrMn_3Mo_6C_{36}H_{65}N_6O_{43}{\cdot}$(2062.36 g/mol): C, 20.97, H, 3.18, N, 4.07, Mo, 27.91, Cr, 2,52, Mn, 7,99. found: C, 20.87, H, 2.80, N, 5.42, Mo, 23.41 (ICP-MS), Cr, 2.13 (ICP-MS), Mn, 7.15 (ICP-MS). TGA (loss of $16H_2O$): calcd. 13.97%, found 12.35%; (loss of $[Mn(1,10\text{-phen})(OH)_2]_3$): calcd. 36.68%, found 35.80%.

$[Co(1,10\text{-phen})(OH)]_3[Cr(OH)_6Mo_6O_{18}]{\cdot}16H_2O$ (3):

Yield: 131 mg, 24%. FT-IR (KBr pellets): υ= 3205 (w), 1622 (s), 1579 (m), 1514 (s), 1424 (s),1344 (m), 1223 (m), 1144 (s), 1104 (s), 944 (s), 913 (m), 849 (m), 776 (m), 727 (m), 642 (m), 565 (m), 413 (m) cm^{-1}. Elem. Anal. Calcd. $CoMn_3Mo_6C_{36}H_{65}N_6O_{43}$ (2074.35 g/mol): C, 20.84, H, 3.16, N, 4.05, Mo, 27.75, Cr, 2,51, Co, 8,52. found: C, 21.94, H, 3.15, N, 4.71, Mo, 24.69 (ICP-MS), Cr, 2.48 (ICP-MS), Co, 8.33 (ICP-MS). TGA (loss of $16H_2O$): calcd. 13.89%, found 12.77%; (loss of $[Co(1,10\text{-phen})(OH)_2]_3$): calcd. 37.04%, found 36.03%.

$[Ni(1,10\text{-phen})(OH)]_3[Cr(OH)_6Mo_6O_{18}]{\cdot}16H_2O$ (4):

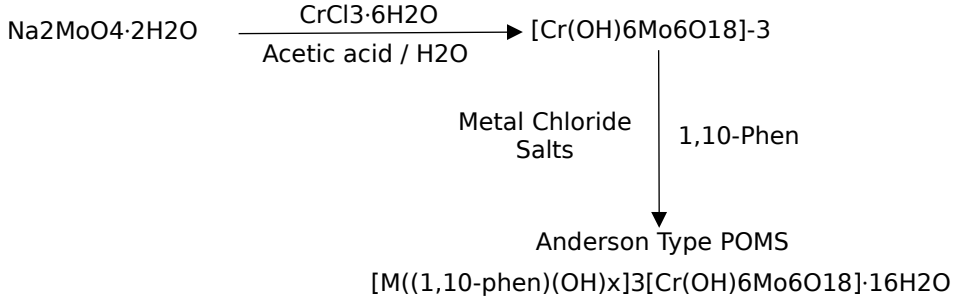
Yield: 108 mg, 20%. FT-IR (KBr pellets): υ= 3065 (w), 1625 (s), 1585 (s), 1517 (s), 1425 (s), 1341 (s), 1225 (s), 1146 (s), 1105 (s), 941 (m), 914 (m), 847 (m), 725 (m), 643 (m), 567 (m), 531 (m), 425 (m) cm^{-1}. Elem. Anal. Calcd. $NiMn_3Mo_6C_{36}H_{65}N_6O_{43}$ (2073.63 g/mol): C, 20.85, H, 3.16, N, 4.05, Mo, 27.76, Cr, 2.51, Ni, 8.49. found: C, 20.35, H, 2.74, N, 4.83, Mo, 26.36 (ICP-MS), Cr, 1.89 (ICP-MS), Ni, 8.34 (ICP-MS). TGA (loss of $16H_2O$): calcd. 13.90%, found 12.35%; (loss of $[Ni(1,10\text{-phen})(OH)_2]_3$): calcd. 37.02%, found 36.00%.

$[Cu(1,10\text{-phen})(OH)]_3[Cr(OH)_6Mo_6O_{18}]{\cdot}16H_2O$ (5):

Yield: 95 mg, 18%. FT-IR (KBr pellets): υ= 3054 (w), 1622 (s), 1518 (s), 1427 (s), 1342 (m), 1309 (m), 1225 (m), 1146 (s), 1107 (s), 915 (s), 890 (m), 842 (m), 772 (m), 722 (m), 643 (m), 496 (m), 427 (m) cm^{-1}. Elem. Anal. Calcd. $CuMn_3Mo_6C_{36}H_{65}N_6O_{43}$ (2088.19 g/mol): C, 20.71, H, 3.14, N, 4.02, Mo, 27.57, Cr, 2,49, Cu, 9,13. found: C, 21.42, H, 2.85, N, 5.32, Mo, 26.89 (ICP-MS), Cr, 2,07 (ICP-MS), Cu, 8,99 (ICP-MS). TGA (loss of $16H_2O$): calcd. 13.80%, found 13.94%; (loss of $[Cu(1,10\text{-phen})(OH)_2]_3$): calcd. 37.46%, found 30.69%.

3. RESULT AND DISCUSSION

A series of new Anderson-type POM compounds $[M((1,10\text{-phen})(OH)_x]_3[Cr(OH)_6Mo_6O_{18}]{\cdot}16H_2O$ (M=Cr(**1**), Mn(**2**), Co(**3**), Ni(**4**), Cu(**5**); x=1,2) were obtained from of $Na_2MoO_4{\cdot}2H_2O$ and $CrCl_3{\cdot}6H_2O$ acidic aqueous medium (Figure 1). It is well known that the stability of polyoxoanions in an aqueous solution depends on the pH. Stability range of $[Cr(OH)_6Mo_6O_{18}]^{3-}$ is 2<pH<3 (20). To obtain this anion it is important to maintain the pH of the solution between 2 and 3 during the addition of the counterion.



Metal	X	Compound No
Cr	2	**1**
Mn	1	**2**
Co	1	**3**
Ni	1	**4**
Cu	1	**5**

Figure 1. Synthesis of new compounds (**1-5**).

The color of the compounds are white (**1**), yellow (**2**), orange (**3**), beige (**4**), and green (**5**). The observed elemental analyses (C, H, N) and ICP-MS (Mo, Cr, Mn, Co, Ni, Cu) data of the new compounds (**1-5**) are in good agreement with the calculated values. Furthermore, experimentally obtained elemental analyses results and other spectroscopic data (FT-IR, ICP-MS, and TGA) support the compounds (**1-5**) formulated as $[M((1,10\text{-phen})(OH)_x]_3[Cr(OH)_6Mo_6O_{18}]\cdot 16H_2O$ (M=Cr(**1**), Mn(**2**), Co(**3**), Ni(**4**), Cu(**5**); x=1,2). Thus, it was determined that the structures of these newly synthesized compounds were similar to the previously reported compounds. (21,22,25,26).

The FT-IR spectra of compounds **1-5** (Supplementary Information Figure S1-S5.) confirms their isostructural nature. The broad bands, respectively 3067 (**1**), 3369 (**2**), 3205 (**3**), 3065 (**4**), and 3054 (**5**) cm^{-1} in the FT-IR spectra of the compounds could be ascribed to O–H bonds, and the bands at 1623,1622 cm^{-1} are attributed to the characteristic of the deformation vibrations of H–O–H of coordinated and lattice-water molecules. The vibrations of compounds **1-5**, ranging from 1107 to 1597 cm^{-1}, are assigned to the 1,10-phenanthroline molecules (20). The vibrations in the range 960-400 cm^{-1} well confirm the Anderson-type cluster $[Cr(OH)_6Mo_6O_{18}]^{3-}$. The bands at 410-940 cm^{-1} are attributed to the vibration modes (Mo-O_t), (Mo-O_b), and (Mo-O_c) of the Anderson anion $[Cr(OH)_6Mo_6O_{18}]^{3-}$. The absorption band at 410-422 cm^{-1} is attributed to the Cr–O. FT-IR results are in agreement with those from previous studies (20-22,25-26).

Thermogravimetric measurements were carried out under a flowing nitrogen atmosphere with a heating rate of 10 °C min^{-1} in 40-800 °C. TGA thermograms of **1** in Figure 2, **2-5** in Supplementary Information Figure S6-S9. As expected, the thermal behavior of compounds **1-5** hasn't been different. The TGA curve of **1** shows (Figure 3), the total weight loss of 16 H_2O (13.16%) in the range of 25–178 °C is attributed to the loss of adsorbed, lattice, coordinated water molecules, and hydroxyls. The second weight loss of 38.07% in the range of 178–704 °C possibly corresponds to the loss of $[Cr(1,10\text{-phen})(OH)_2]_3$ group. Table 1 shows the results of the TGA analysis. TGA results are in agreement with those from previous studies (20-22,25-26).

Table 1. Results of the TGA analysis.

Compound	Losses Part	Calc. (%)	Exp. (%)	Losses Part	Calc. (%)	Exp. (%)
1	$16H_2O$	13.69	13.16	$[Cr(1,10\text{-phen})(OH)_2]_3$	37.95	38.07
2	$16H_2O$	13.97	12.35	$[Mn(1,10\text{-phen})(OH)]_3$	36.68	35.80
3	$16H_2O$	13.89	12.77	$[Co(1,10\text{-phen})(OH)]_3$	37.04	36.03
4	$16H_2O$	13.90	12.35	$[Ni(1,10\text{-phen})(OH)]_3$	37.02	36.00
5	$16H_2O$	13.80	13.94	$[Cu(1,10\text{-phen})(OH)]_3$	37.46	30.69

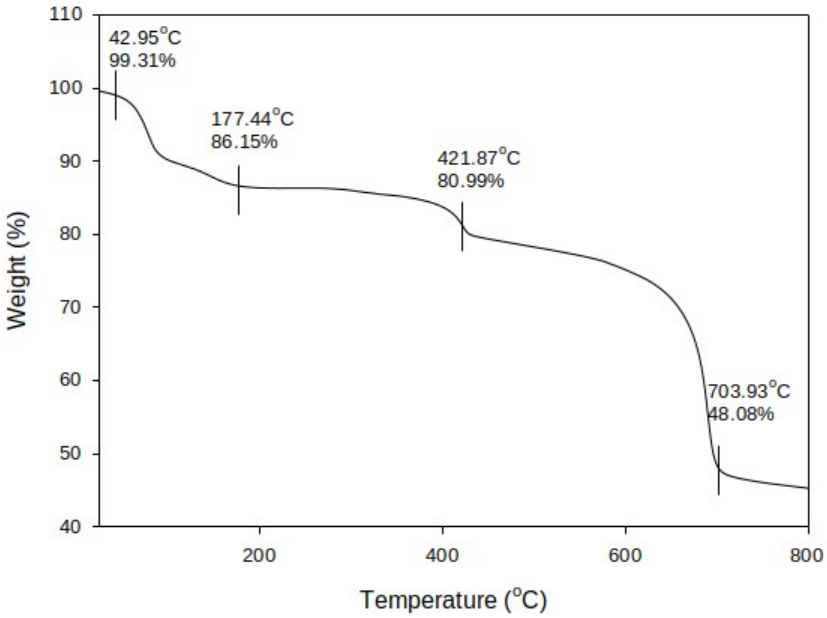


Figure 2. TGA spectrum of **1**.

4. CONCLUSION

In this paper, the structural characterization of newly synthesized Anderson-type POMs: $[M((1,10\text{-phen})(OH)_x]_3[Cr(OH)_6Mo_6O_{18}]\cdot 16H_2O$ (M=Cr(**1**), Mn(**2**), Co(**3**), Ni(**4**), Cu(**5**); x=1,2) were carried out using FT-IR, elemental analysis, ICP-MS, and TGA methods. Since the low solubility of the compounds in organic solvents and insoluble in water, other spectroscopic methods (NMR, ESI) could not be used in structural characterization and crystal suitable for X-Ray analysis could not be obtained.

5. CONFLICT OF INTEREST

There is no conflict of interest.

6. ACKNOWLEDGMENTS

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SUPPLEMENTARY INFORMATION

Synthesis and Characterization of New Anderson-Type Polyoxometalates: $[M((1,10\text{-phen})(OH)_x]_3[Cr(OH)_6Mo_6O_{18}]\cdot 16H_2O$ (M=Cr, Mn, Co, Ni, Cu; x=1,2)

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FT-IR Spectrum

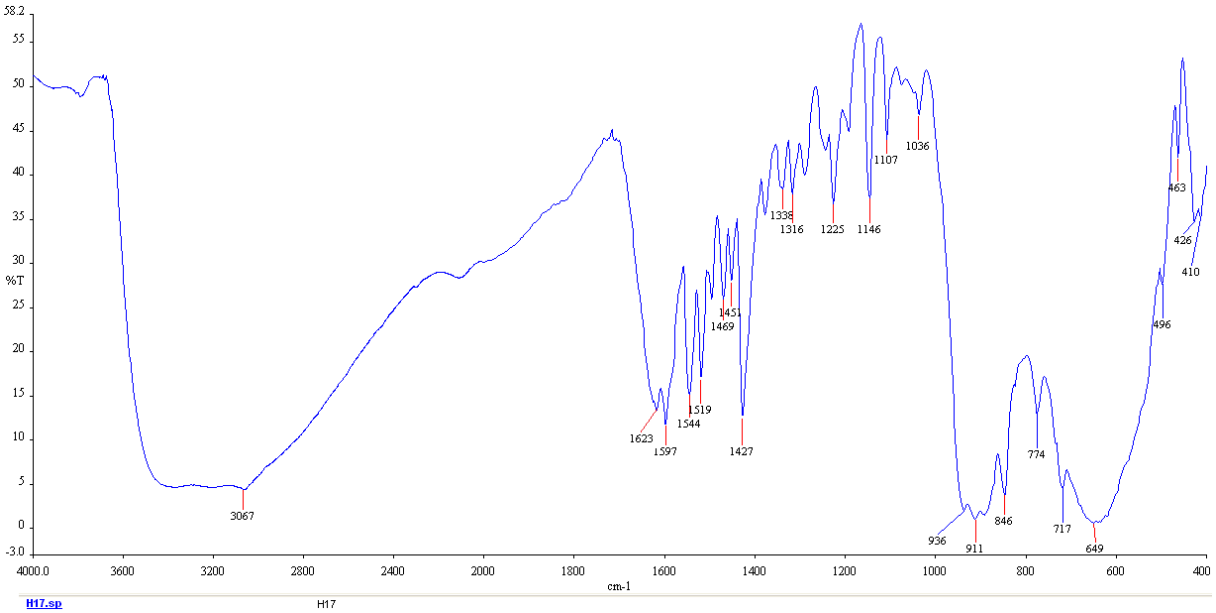

Figure S 1. FT-IR Spectrum of **1**

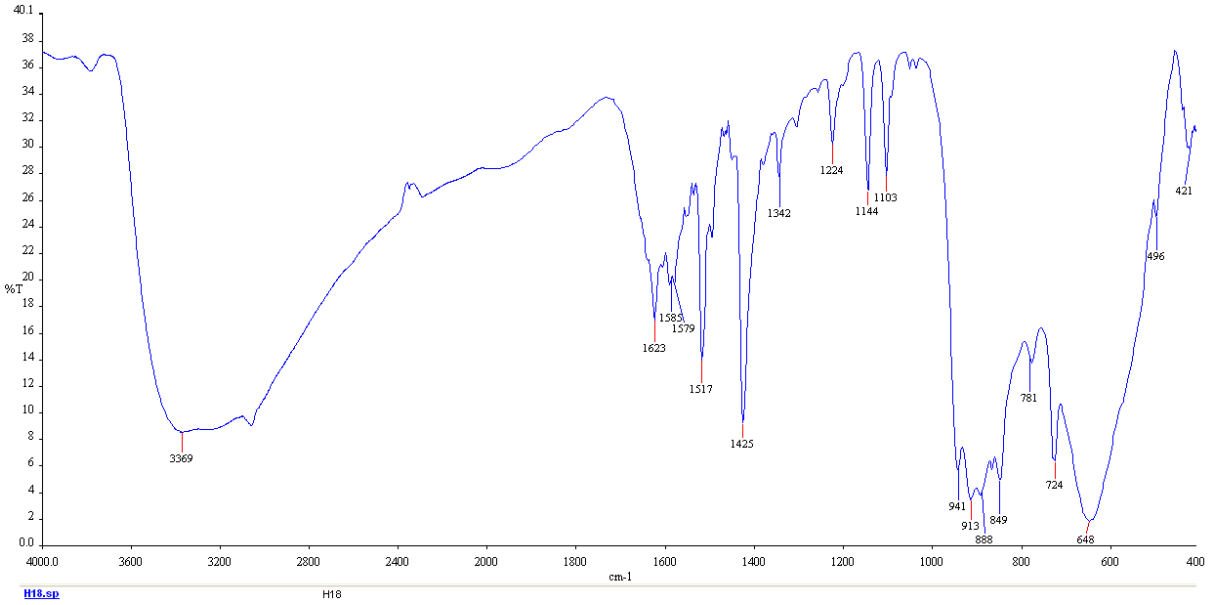

Figure S 2. FT-IR Spectrum of **2**

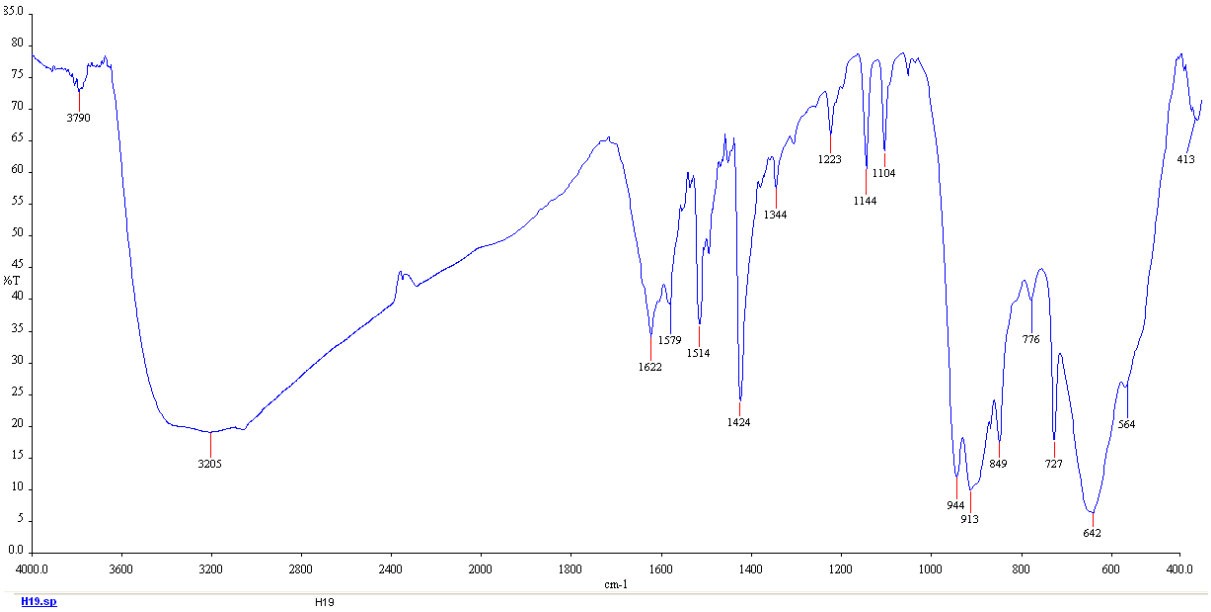

Figure S 3. FT-IR Spectrum of **3**

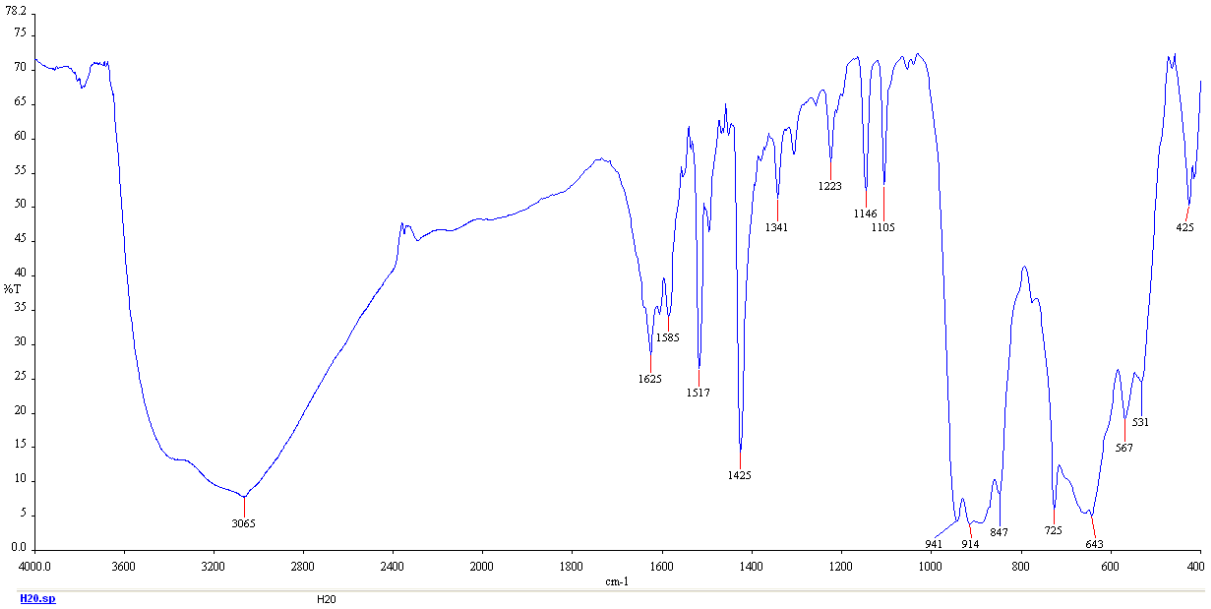

Figure S 4. FT-IR Spectrum of **4**

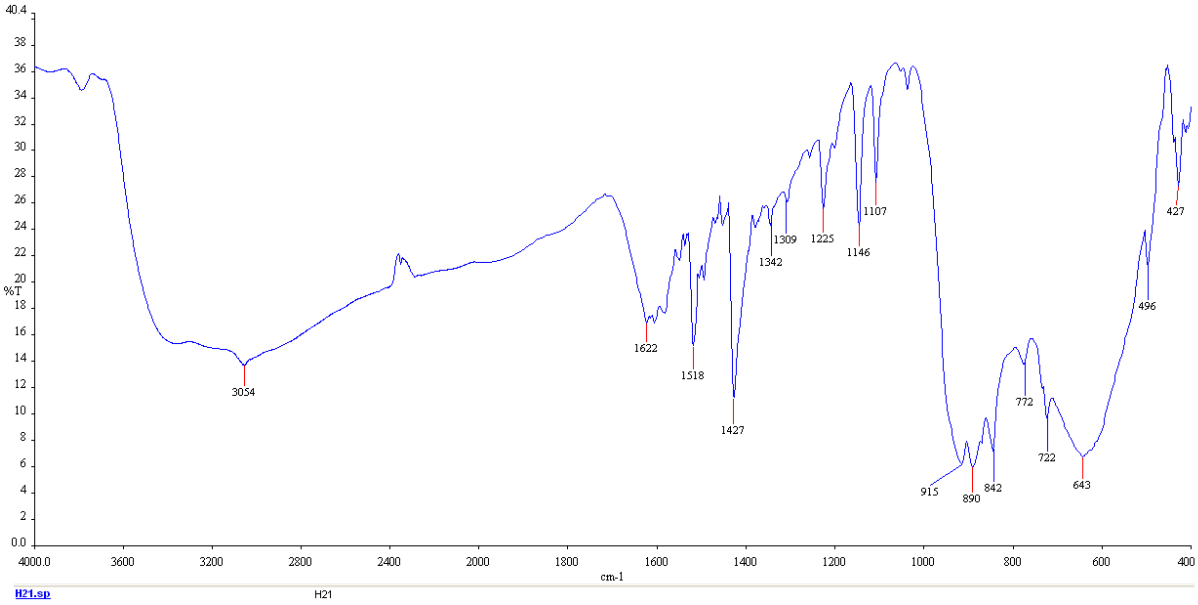

Figure S 5. FT-IR Spectrum of **5**

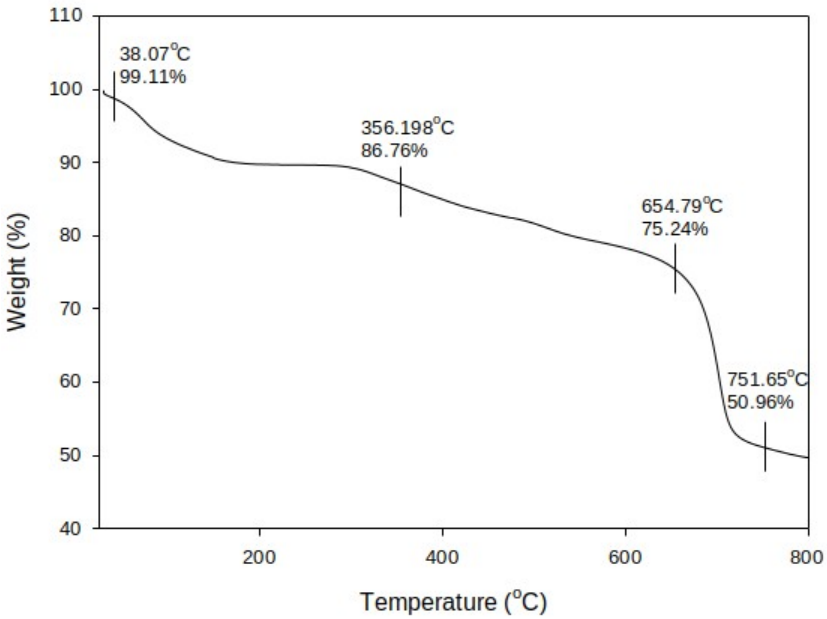

Figure S 6. TGA spectrum of **2**

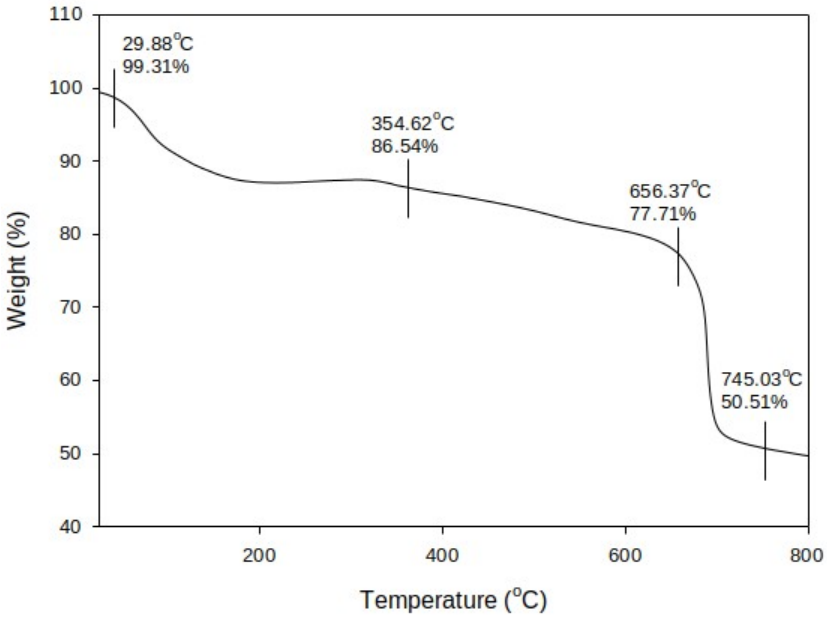

Figure S 7. TGA spectrum of **3**

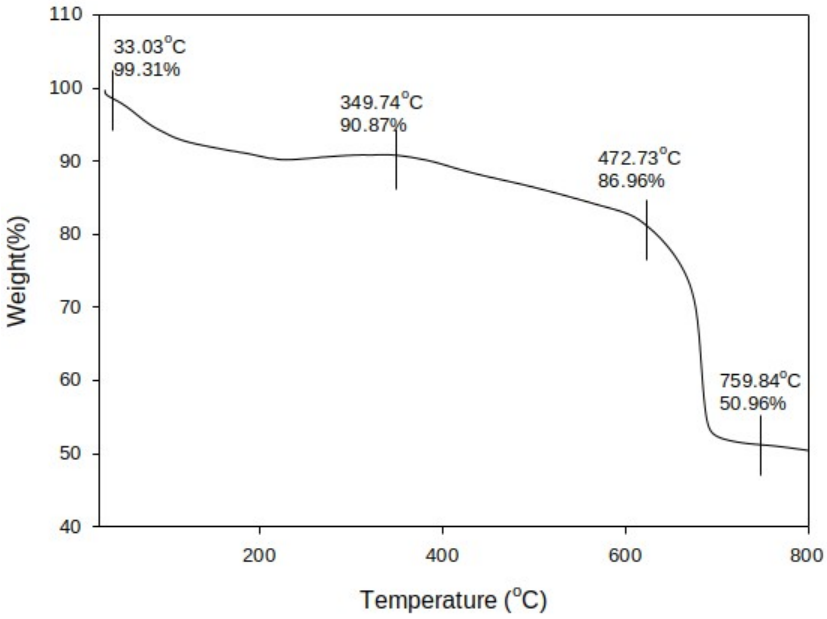

Figure S 8. TGA spectrum of **4**

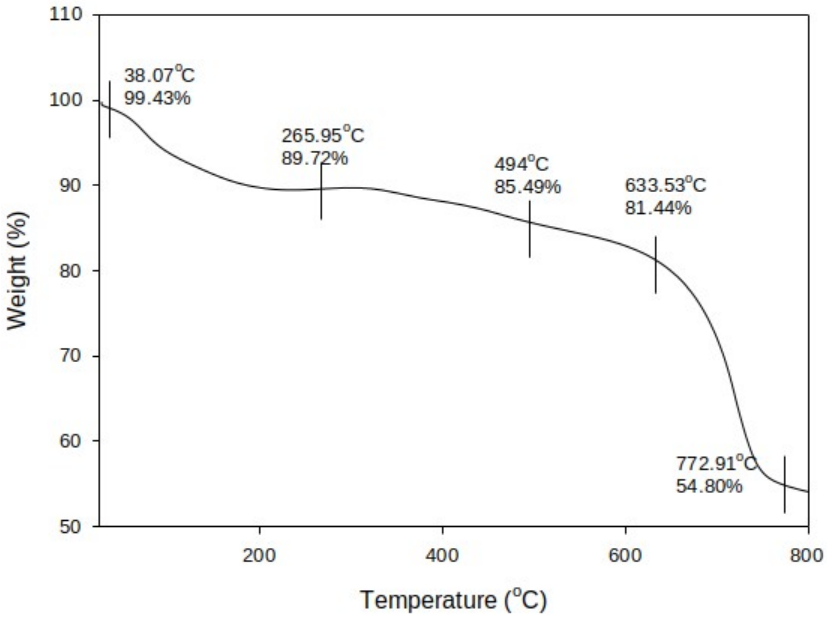

Figure S 9. TGA spectrum of **5**