

Syntheses, structures and properties of a series of nickel(II) complexes derived from amino-5-mercapto-1,3,4-thiadiazole

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Abstract

Four complexes possessing photocatalytic activity, namely $[Ni(AMT)_2(EDA)_2]_2$ (1), $[Ni_4(AMT)_6(\mu_3-OH)_2(H_2O)_6]$ (2), $[Ni_4(AMT)_6(\mu_3-OH)_2(H_2O)_6] \cdot 4H_2O$ (3) and $[Ni_4(AMT)_6(\mu_3-OH)_2(H_2O)_6] \cdot 2H_2O$ (4) (AMT = amino-5-mercapto-1,3,4-thia-diazole and EDA = diethanolamine) have been obtained from solvothermal reactions and characterized by physico-chemical and spectroscopic methods. Although complexes 1–4 were prepared from common reactants (nickel nitrate and AMT), the use of different organic amines and reaction conditions lead to the observed differences in their structures. Complex 1 is mononuclear, while complex 2 is a $\{Ni_4\}$ cluster. Complexes 3–4 are expanded into supramolecular structures by hydrogen bonding interactions, but differences in their lattice water molecules lead to the different supramolecular structures. Photocatalytic studies reveal that complex 4 exhibits good catalytic activity for the degradation of the organic dye methylene blue.

Introduction

In recent years, much attention has been focused on the design and construction of novel complexes with interesting properties in the fields of fluorescence [1-3], catalysis [4, 5], magnetism [6–8], electrochemistry [9–11] and gas adsorption/separation [12, 13]. Among these properties, photocatalytic complexes have potential applications in the remediation of environmental pollution [14–16]. Industrial activity has released many harmful pollutants into the environment, which are bad for health and economic development [17–19]. As one such class of pollutants, organic dyes are difficult to remove by conventional methods because of their stable chemical and non-biodegradable properties. Hence, there is an urgent need to find effective methods for the degradation of these organic pollutants. In recent years, many research groups have studied photocatalytic degradation, which has great potential for decomposition of organic dyes [20–22]. Liu et al. synthesized a variety of cobalt(II)

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coordination polymers which show photocatalytic activities for the degradation of methylene blue (MB) [20]. Fan et al. obtained two-dimensional layered complexes that exhibit preeminent catalytic performance for the homo-coupling of aryl bromides or iodides without by-products [21]. Therefore, research into metal organic complexes possessing good catalytic properties is a current area of interest.

Transition metal-oxygen clusters have become an important research field in both coordination chemistry and crystal engineering because of their fascinating structures and potential applications [23–28]. In these materials, the organic ligands play a crucial role in their structures. As functional ligands, thiol-containing azaheterocyclic ligands have three advantages. Firstly, the thiol group allows for conformational rotation, allowing for flexible complex geometries. Secondly, these ligands have multiple coordination sites, due to the two nitrogen atoms of the thiadiazole group and the thiolate sulfur atom. Hence, they are likely to have a wealth of chemical properties [29–31].

In this work, we selected the late transition metal nickel(II), together with 2-amino-5-mercapto-1,3,4-thiadiazole (AMT) to obtain four new mononuclear and tetranuclear clusters, namely $[Ni(AMT)_2(EDA)_2]_2$ (1), $[Ni_4(AMT)_6(\mu_3-OH)_2(H_2O)_6]$ (2), $[Ni_4(AMT)_6(\mu_3-OH)_2(H_2O)_6]\cdot 4H_2O$ (3) and $[Ni_4(AMT)_6(\mu_3-OH)_2(H_2O)_6]\cdot 2H_2O$ (4). The influence of organic amines and different reaction temperatures on the products is discussed. In addition, the photocatalytic

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properties of complex **4** have been investigated, revealing that complex **4** is able to degrade MB.

Experimental

Materials and methods

All reagents were purchased commercially and used without further purification. Elemental analyses (C, H, N) were obtained with a PerkinElmer 2400 CHN elemental analyzer. FTIR spectra (KBr pellets) were taken on a Nicolet 170SX spectrophotometer. Thermogravimetric (TG) analyses were carried out on an Exstar SII TG/DTA 7200 integration thermal analyzer. Powder X-ray diffraction (PXRD) patterns were measured on a Siemens D5005 diffractometer (Cu Ka radiation, $\lambda = 1.5410$ Å). UV–vis absorption spectra were recorded on a TU-1901 UV–vis spectrophotometer.

Synthesis of complex 1

A mixture of Ni(NO₃)₂·6H₂O (0.2908 g, 1.00 mmol), **AMT** (0.1332 g, 1.00 mmol), distilled water (4 mL) and ethanol (4 mL) was transferred to a 25-mL Teflon-lined reactor. Ethylenediamine (1.5 mL) was then added to the reaction solution under stirring, keeping the mixture at 110 °C for 3 days. After cooling the autoclave to room temperature, green block crystals were obtained, but with poor reproducibility and crystallinity. Yield 15% based on Ni(II). Elemental analysis (%) calcd for $C_{16}H_{40}N_{20}Ni_2S_8$: C, 21.68; H, 4.55; N, 31.60%. Found: C, 21.64; H, 4.53; N, 31.58%. IR (KBr pellet, cm⁻¹): 3225(m), 1596(s), 1514(s), 1454(m), 1374(s), 1326(s), 1263(m), 1117(w), 1008(s), 947(s), 872(w), 755(s), 673(s), 614(w), 594(w), 576(w), 517(m).

Synthesis of complex 2

The synthesis of complex **2** was similar to that of **1**, except that the ethylenediamine was replaced by triethanolamine. Green block crystals were obtained. Yield 23% based on Ni(II). Elemental analysis (%) calcd for $C_{12}H_{26}N_{18}Ni_4O_8S_{12}$:

Complex	1	2	3	4
Empirical formula	C ₁₆ H ₄₀ N ₂₀ Ni ₂ S ₈	C ₁₂ H ₂₆ N ₁₈ Ni ₄ O ₈ S ₁₂	C ₁₂ H ₃₄ N ₁₈ Ni ₄ O ₁₂ S ₁₂	C ₁₂ H ₃₀ N ₁₈ Ni ₄ O ₁₀ S ₁₂
Formula weight	886.58	1170.07	1242.13	1206.08
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/n	P2(1)/n	P2(1)/n
a (Å)	8.6276(11)	10.5052(11)	13.4656(11)	10.4245(6)
<i>b</i> (Å)	10.1567(12)	9.5476(9)	9.6485(6)	9.4637(6)
<i>c</i> (Å)	11.3063(15)	19.780(2)	17.2696(12)	19.7434(10)
α (°)	90	90	90	90
β (°)	99.458(13)	95.356(9)	90.0890(10)	95.0900(10)
γ (°)	90	90	90	90
$V(\text{\AA}^3)$	977.3(2)	1975.3(3)	2243.7(3)	1940.09(19)
Ζ	1	2	2	4
$Dc (g \text{ cm}^{-3})$	1.506	1.967	1.839	2.061
$\mu (\text{mm}^{-1})$	1.432	2.575	2.279	2.628
F (000)	460	1184	1264	1220
Reflection collected	6056	8405	5698	11,092
Unique reflections	1724	3488	3398	3423
Parameters	106	244	262	253
R _{int}	0.0554	0.0762	0.0408	0.0556
GOF	1.045	1.045	1.036	1.068
$R_1^{\rm a}\left[I > 2\sigma(I)\right]$	0.0424	0.0543	0.0639	0.0367
wR_2^{b} (all data)	0.1130	0.0923	0.1682	0.0930

 ${}^{a}R_{1} = \Sigma ||Fo| - |Fc|| / \Sigma |Fo|$

 ${}^{b}wR_{2} = \Sigma[w(Fo^{2}-Fc^{2})^{2}]/\Sigma[w(Fo^{2})^{2}]^{1/2}$

Table 2Selected bond distances(Å) and angles (deg) forcomplexes 1-4

Complex 1			
Ni(1)–N(5)#1	2.098(3)	Ni(1)-N(4)#1	2.111(3)
Ni(1)–N(5)	2.098(3)	Ni(1)-N(1)#1	2.132(3)
Ni(1)–N(4)	2.111(3)	Ni(1)–N(1)	2.132(3)
N(5)#1-Ni(1)-N(5)	180.0(2)	N(4)-Ni(1)-N(1)#1	90.55(13)
N(5)#1-Ni(1)-N(4)	82.31(13)	N(4)#1-Ni(1)-N(1)#1	89.45(13)
N(5)–Ni(1)–N(4)	97.69(13)	N(5)#1-Ni(1)-N(1)	91.09(12)
N(5)#1-Ni(1)-N(4)#1	97.69(13)	N(5)-Ni(1)-N(1)	88.91(12)
N(5)-Ni(1)-N(4)#1	82.31(13)	N(4)-Ni(1)-N(1)	89.45(13)
N(4)-Ni(1)-N(4)#1	180.00(18)	N(4)#1-Ni(1)-N(1)	90.55(13)
N(5)#1-Ni(1)-N(1)#1	88.91(12)	N(1)#1-Ni(1)-N(1)	180.0(3)
N(5)-Ni(1)-N(1)#1	91.09(12)		
Symmetry codes for 1: $\#1 - x + 1$, $-y$, $-z$			
Complex 2			
Ni(1)-O(1)	2.028(4)	Ni(2)–O(1)	2.009(4)
Ni(1)–O(1)#1	2.038(4)	Ni(2) - N(2)	2.095(5)
Ni(1)–N(7)	2.099(5)	Ni(2) - N(4)	2.098(5)
Ni(1)-N(1)	2.101(5)	Ni(2) - O(4)	2.105(4)
Ni(1) - N(5)	2.102(5)	Ni(2) - O(3)	2.170(4)
Ni(1) - O(2)	2.120(4)	Ni(2) - S(6) #1	2.4707(19)
O(1) - Ni(1) - O(1) # 1	82.06(16)	O(1) - Ni(2) - N(2)	90.84(18)
O(1) - Ni(1) - N(7)	92.86(18)	O(1) - Ni(2) - N(4)	85 19(18)
O(1)#1-Ni(1)-N(7)	93 24(18)	N(2) - Ni(2) - N(4)	89 4(2)
O(1) - Ni(1) - N(1)	88 50(18)	$\Omega(1) - Ni(2) - \Omega(4)$	89.93(17)
O(1) # 1 - N(1) - N(1)	89.46(18)	N(2) - Ni(2) - O(4)	179.22(19)
N(7) - N(1) - N(1)	177 1(2)	N(2) = Ni(2) = O(4) N(4) = Ni(2) = O(4)	90.6(2)
O(1) N(1) N(5)	80 56(18)	O(1) Ni(2) $O(3)$	90.0(2) 173 58(16)
O(1) + 1 N(1) - N(5)	171.45(10)	N(2) Ni(2) O(3)	04.01(10)
N(7) N(1) N(5)	28 0(2)	N(2) = N(2) = O(3) N(4) = N(2) = O(3)	94.91(19)
N(1) = N(1) = N(3) N(1) = N(3)	88.9(2)	N(4) = NI(2) = O(3)	92.00(18)
N(1) - N(1) - N(3) O(1) N(1) O(2)	177.06(16)	O(4) = NI(2) = O(3) O(1) = NI(2) = S(6) # 1	04.32(10)
O(1) + IN(1) - O(2)	05 15(15)	O(1) = NI(2) = S(6) #1	94.62(12)
V(1)#1-N(1)-O(2)	95.15(15)	N(2) = NI(2) = S(6) # 1	91.02(13)
N(7) - NI(1) - O(2)	88.24(18)	N(4) - NI(2) - S(6) + 1	1/8.9/(10)
N(1) - N(1) - O(2) N(5) - N'(1) - O(2)	90.32(18)	O(4) - NI(2) - S(6) + 1 O(2) NI(2) - S(6) + 1	88.32(13) 97.99(12)
N(3) = NI(1) = O(2)	95.19(19)	O(3) - NI(2) - S(0) + 1	87.88(13)
Symmetry codes for 2: $\#1 - x + 1$, $-y + 1$, $-z + 1$			
Complex 3	2.047(5)	N:(2) O(1)	2 009(5)
NI(1) = O(1)	2.047(5)	NI(2) = O(1)	2.008(5)
NI(1)-O(1)#1	2.051(5)	NI(2) - N(1)	2.102(7)
$N_1(1) - N(7) \# 1$	2.091(6)	Ni(2) - N(5)	2.108(6)
$N_1(1) - N(4)$	2.094(6)	$N_1(2) = O(3)$	2.125(5)
$N_1(1)-O(2)$	2.115(5)	N1(2)–O(4)	2.148(5)
Ni(1)-N(2)	2.139(7)	Ni(2)-S(6)	2.474(2)
O(1)-Ni(1)-O(1)#1	83.0(2)	O(1) - Ni(2) - N(1)	86.4(2)
O(1)–Ni(1)–N(7)#1	92.9(2)	O(1) - Ni(2) - N(5)	91.6(2)
O(1)#1–Ni(1)–N(7)#1	91.6(2)	N(1)-Ni(2)-N(5)	88.3(3)
O(1)–Ni(1)–N(4)	88.5(2)	O(1)-Ni(2)-O(3)	173.8(2)
O(1)#1–Ni(1)–N(4)	90.5(2)	N(1)-Ni(2)-O(3)	93.0(2)
N(7)#1–Ni(1)–N(4)	177.7(3)	N(5)–Ni(2)–O(3)	94.5(2)
O(1)–Ni(1)–O(2)	177.5(2)	O(1)-Ni(2)-O(4)	88.1(2)
O(1)#1–Ni(1)–O(2)	94.5(2)	N(1)-Ni(2)-O(4)	90.2(2)
N(7)#1-Ni(1)-O(2)	87.0(2)	N(5)-Ni(2)-O(4)	178.5(2)

Table 2 (continued)

N(4)–Ni(1)–O(2)	91.7(2)	O(3)–Ni(2)–O(4)	85.7(2)
O(1)–Ni(1)–N(2)	88.8(2)	O(1)-Ni(2)-S(6)	93.93(16)
O(1)#1-Ni(1)-N(2)	171.8(2)	N(1)-Ni(2)-S(6)	178.69(18)
N(7)#1-Ni(1)-N(2)	89.1(3)	N(5)-Ni(2)-S(6)	93.02(19)
N(4)-Ni(1)-N(2)	89.1(3)	O(3)-Ni(2)-S(6)	86.59(17)
O(2)-Ni(1)-N(2)	93.7(2)	O(4)-Ni(2)-S(6)	88.52(17)
Symmetry codes for 3 : $\#1 - x + 1$, $-y + 1$, $-z + 1$			
Complex 4			
Ni(1)–O(1)	2.042(3)	Ni(2)–O(1)	2.009(3)
Ni(1)-O(1)#1	2.048(3)	Ni(2)–N(1)	2.090(4)
Ni(1)–N(7)	2.086(4)	Ni(2)–O(4)	2.099(3)
Ni(1)–N(4)	2.088(4)	Ni(2)–N(5)	2.104(4)
Ni(1)–O(2)	2.111(3)	Ni(2)–O(3)	2.160(3)
Ni(1)–N(2)	2.122(4)	Ni(2)-S(6)#1	2.4723(13)
O(1)–Ni(1)–O(1)#1	83.33(13)	O(1)-Ni(2)-N(1)	84.89(13)
O(1)-Ni(1)-N(7)	91.98(14)	O(1)-Ni(2)-O(4)	89.40(13)
O(1)#1-Ni(1)-N(7)	93.14(13)	N(1)-Ni(2)-O(4)	91.03(14)
O(1)–Ni(1)–N(4)	88.96(13)	O(1)-Ni(2)-N(5)	91.42(14)
O(1)#1-Ni(1)-N(4)	89.46(13)	N(1)-Ni(2)-N(5)	89.24(15)
N(7)–Ni(1)–N(4)	177.32(13)	O(4)-Ni(2)-N(5)	179.16(14)
O(1)–Ni(1)–O(2)	177.37(12)	O(1)-Ni(2)-O(3)	173.05(13)
O(1)#1-Ni(1)-O(2)	94.04(12)	N(1)-Ni(2)-O(3)	92.66(14)
N(7)-Ni(1)-O(2)	88.04(14)	O(4)-Ni(2)-O(3)	84.13(12)
N(4)-Ni(1)-O(2)	91.14(14)	N(5)-Ni(2)-O(3)	95.06(14)
O(1)-Ni(1)-N(2)	88.96(13)	O(1)-Ni(2)-S(6)#1	94.57(9)
O(1)#1-Ni(1)-N(2)	171.96(14)	N(1)-Ni(2)-S(6)#1	179.23(11)
N(7)-Ni(1)-N(2)	89.40(14)	O(4)-Ni(2)-S(6)#1	88.41(9)
N(4)-Ni(1)-N(2)	88.10(14)	N(5)-Ni(2)-S(6)#1	91.33(10)
O(2)–Ni(1)–N(2)	93.67(14)	O(3)-Ni(2)-S(6)#1	87.81(9)
Symmetry codes for 4: $\#1 - x + 1$, $-y + 1$, $-z + 1$			

 Table 3
 Data of hydrogen bounds for complexes 3–4

D–H···A	D–H	Н…А	D…A	D–H…A
Complex 3				
$N(3)-H(3B)-O(5W)^{a}$	0.86	2.11	2.9360	162
O(4W)-H(3D)O(2W) ^b	0.85	2.26	3.0647	157
O(3W)-H(4B)O(5W)	0.85	2.14	2.9777	168
O(3W)-H(4C)O(3W) ^c	0.85	2.25	3.0772	164
O(4W)- $H(5A)$ ···N(9) ^d	0.85	2.20	2.9172	142
$O(4W)-H(5C)\cdots O(4W)^b$	0.85	2.01	2.8193	159
Symmetry codes for 3 : a $1/(-z)$; c - x, 1 - y, -z; d 1	2 - x, 1/2 /2 - x, -	2 + y, 1/2 - 1/2 + y, 1/2	z; b 1 - x, 2 - z	1 – y,
Complex 4				
O(1W)-H(2B)-O(3W) ^a	0.85	2.55	3.0237	117
$N(9)$ – $H(9A)$ ···O $(4W)^b$	0.86	2.22	2.9803	147
Symmetry codes for 4 : a x ,	-1 + y,	z; b 1 - x,	1 - y, 1 - z	5

C, 12.32; H, 2.24; N, 21.55%. Found: C, 12.29; H, 2.22; N, 21.53%. IR (KBr pellet, cm⁻¹): 3515(m), 3435(m), 3139(s), 2361(w), 1597(s), 1522(s), 1402(s), 1355(m), 1309(w), 1053(s), 933(m), 718(m), 624(w), 557(w).

Synthesis of complex 3

The synthetic method for complex **3** was similar to that of **1**, except that the ethylenediamine was replaced by triethylamine/ethanolamine in 4:1 ratio (v/v). Green block crystals were obtained. Yield 28% based on Ni(II). Elemental analysis (%) calcd for $C_{12}H_{34}N_{18}Ni_4O_{12}S_{12}$: C, 11.60; H, 2.76; N, 20.30%. Found: C, 11.57; H, 2.74; N, 20.33%. IR (KBr pellet, cm⁻¹): 3567(m), 3412(m), 3147(s), 1615(s), 1574(m), 1532(s), 1421(s), 1372(m), 1066(m), 916(w), 723(m), 673(m), 661(w), 624(w), 531(m), 508(w).



Fig. 1 a Coordination environment of the Ni atom in complex 1 (#1 -x + 1, -y, -z). **b** The mononuclear structure for **1**

Synthesis of complex 4

The synthetic method for complex **4** was similar to that of **3**, except that the reaction temperature was maintained at 130 °C for 3 days. Green block crystals were obtained. Yield 25% based on Ni(II). Elemental analysis (%) calcd for $C_{12}H_{30}N_{18}Ni_4O_{10}S_{12}$: C, 11.95; H, 2.51; N, 20.90%. Found: C, 11.97; H, 2.54; N, 20.93%. IR (KBr pellet, cm⁻¹): 3523(m), 3446(m), 3158(s), 1603(s), 1560(m), 1527(s), 1410(s), 1358(m), 1053(m), 927(w), 716(m), 665(m), 656(w), 613(w), 561(m), 511(w).

X-ray crystallographic studies

Single-crystal X-ray diffraction data collections for complexes 1-4 were carried on a Bruker APEX diffractometer with Mo Ka radiation (graphite monochromator, $\lambda = 0.71073$ Å) at 298 K. The structures were solved by direct methods using the SHELXTL crystallographic software package and refined by full-matrix least squares methods on F^2 with SHELXL [32]. In final refinements for complexes 1-4, all nonhydrogen atoms were refined anisotropically. The carbon, nitrogen and oxygen-bound hydrogen atoms were generated theoretically onto the specific atoms and refined isotropically using fixed thermal factors. Summaries of the crystallographic data and structure refinement parameters for complexes 1-4 are listed in Table 1. Selected bond distances and angles are given in Table 2. The hydrogen bond parameters are summarized in Table 3. The CCDC numbers are 1470863-1470866 for complexes 1-4.



Fig. 2 Coordination environment of Ni atom in complex 2 (#1 -x + 1, -y + 1, -z + 1)





Fig. 3 a Unit of binuclear for 2. b The tetranuclear clusters for 2

Results and discussion

Crystal structure of [Ni(AMT)₂(EDA)₂]₂ (1)

The single-crystal X-ray diffraction study shows that complex **1** crystallizes in the monoclinic P2(1)/c space group. The asymmetric unit contains two crystallographically independent nickel atoms, four **AMT** ligands and four ethylenediamine ligands. The Ni1 is located in an octahedral configuration, being coordinated by two nitrogen atoms (N1, N1#1) from the 1,3,4-thiadiazole groups of the **AMT** ligands, plus four nitrogen atoms (N4, N5, N4#1 and N5#1) of two ethylenediamine ligands (Fi. 1a). The Ni–N bond lengths are in the range of 2.098(3)–2.132(3) Å. Complex **1** has a mononuclear structure (Fig. 1b), which can be explained by the chelating ability of the ethylenediamine ligands.

Crystal structure of $[Ni_4(AMT)_6(\mu_3-OH)_2(H_2O)_6]$ (2)

Complex 2 crystallizes in the monoclinic P2(1)/n space group. The asymmetric unit includes two nickel atoms, three **AMT** ligands, one μ_3 -bridging hydroxyl group and three water ligands. The Ni centers all have octahedral geometries, with two kinds of coordination environment. Ni1 is coordinated by three nitrogen atoms (N2, N4 and N7) from the 1,3,4-thiadiazole groups of three separate **AMT** ligands, two oxygen atoms (O1 and O1#1) of μ_3 -bridging hydroxyl groups and one water ligand (O1W) (Fig. 2a). Ni2 is coordinated by two nitrogen atoms (N1 and N5) from the 1,3,4-thiadiazole groups of two separate AMT ligands, one sulfur atom (S6) from one thiol group of an AMT ligand, one oxygen atom (O1) of a μ_3 -bridging hydroxyl group and two water ligands (O2W and O3W) (Fig. 2b). The Ni-O, Ni-N and Ni–S bond lengths are in the ranges of 2.009(4)–2.170(4) Å, 2.095(5)-2.102(5) Å and 2.4707(19) Å, respectively. The AMT ligands display two types of coordination patterns. In the first, two nitrogen atoms of the 1,3,4-thiadiazole groups are coordinated to the metal. In the second, one nitrogen atom of a 1,3,4-thiadiazole group and one thiolate sulfur atom are coordinated. Four AMT ligands serve to connect two Ni atoms, forming a binuclear structure, in which the two metal Ni atoms exhibit vertices sharing (Fig. 3a). Pairs of binuclear units are interconnected by hydroxylic oxygen atoms to form a tetranuclear cluster, exhibiting side-sharing (Fig. 3b).

Crystal structure of $[Ni_4(AMT)_6(\mu_3-OH)_2(H_2O)_6]\cdot 4H_2O$ (3)

Although the core structure of complex **3** is the same as that of complex **2**, the tetranuclear clusters are expanded into a 3D supramolecular framework by hydrogen bonding interactions in complex **3**. Thus, 2D layers are formed through three kinds of $O-H\cdots O$ hydrogen bonding interactions, between the neighboring lattice water molecules (O4W), between the lattice water molecules (O4W) and the water ligands (O2W), and between the water

Fig. 4 a 2D structure of complex **3. b** View of 3D supramolecular framework of **3**



(a)







ligands (O3W) (Fig. 4a) $[O(4W)-H(5C)\cdots O(4W) = 2.8$ 193 Å, O(4W)-H (3D) $\cdots O(2W) = 3.0647$ Å, O(3W)-H(4C) $\cdots O(3W) = 3.0772$ Å]. The adjacent 2D supramolecular layers are extended into a 3D supramolecular framework by hydrogen bonding interactions from the water ligand (O3W) and the lattice water molecules (O5W) with a distance of 2.9777 Å. The other hydrogen bonding interactions are between the nitrogen atoms (N3 and N9) of the **AMT** ligands and the lattice water molecules (O5W and O4W) [N(3)-H(3B) $\cdots O(5W) = 2.9360$ Å and N(9)-H(5A) $\cdots O(4W) = 2.9172$ Å] (Fig. 4b).

Crystal structure of $[Ni_4(AMT)_6(\mu_3-OH)_2(H_2O)_6]\cdot 2H_2O$ (4)

In contrast to complex **3**, in complex **4** the tetranuclear clusters are extended into a 2D supramolecular network by hydrogen bonding interactions. The adjacent tetranuclear clusters are interconnected by hydrogen bonding interactions between two water ligands (O1W and O3W), with an O(1W)–H(2B)···O(3W) distance of 3.0237 Å, to form a 1D supramolecular chain. Neighboring chains are assembled into a 2D supramolecular network through hydrogen bonding interactions between the lattice water molecules (O4W) and the nitrogen atoms (N9) from the **AMT** ligands [N(9)–H(9A)···O(4W) = 2.9803 Å] (Fig. 5).



Fig. 6 Summary vision of structure for complexes 1-4



Fig. 7 TG curves of the complexes 1-4 under N₂ atmosphere

Influence of amines and reaction temperature

Although the syntheses of all four complexes use nickel nitrate and AMT, different organic amines and reaction temperatures were used. These differences determine the structures of complexes (Fig. 6). Firstly, in the syntheses of complexes 1-3, the amines were ethylenediamine, triethanolamine and a mixture of triethylamine and ethanolamine, respectively. Complex 1 is a mononuclear structure; it appears that the strong chelating effect of ethylenediamine restricts further expansion of the structure. Complexes 2 and 3 are both tetranuclear clusters, but with differences in the lattice water molecules. Thus, there are no weak interactions in complex 2 because of the absence of the lattice water. However, in complex 3, there are four lattice water molecules around each tetranuclear cluster, leading to formation of the final 3D supramolecular framework by hydrogen bonding interactions.

For complexes **3** and **4**, the organic amines were the same, but the different reaction temperatures led to differences in



Fig. 8 Absorption spectra of the MB solution during the decomposition reaction with the presence of complex 4



Fig. 9 Photocatalytic decomposition rates of MB solution under visible light irradiation with the use of the complex 4 and the control experiment without any catalyst

the final supramolecular structures. Complex **3** was obtained at 110 °C and complex **4** at 130 °C. Although both complexes are tetranuclear clusters, there is only one lattice water molecule for each tetranuclear cluster of complex **4**, which affects the further expansion of the 2D supramolecular structure.

X-ray powder diffraction and thermal stabilities

The X-ray powder diffraction (XRPD) patterns for complexes 1–4 were obtained at room temperature. As shown in Fig. S2, the patterns for the experimental samples match with the simulated ones, confirming the phase purities of the samples. The differences of intensity may be caused by the preferred orientation of the crystals [33].

In order to investigate the thermal stabilities of the complexes, TG analyses were carried out in a flowing nitrogen atmosphere between 30 and 800 °C, at a heating rate of 10 °C min⁻¹ (Fig. 7). Complex 1 only displays one weight loss step, while complexes 2–4 show two weight loss steps. For complex 1, the main skeleton began to collapse at 220 °C, with a total weight loss of 74.47%. The first weight losses for the other complexes are 11.64% at 150-220 °C for **2**, 8.66% at 130–210 °C for **3** and 12.10% at 120–225 °C for 4. These can be assigned to the loss of hydroxyl groups and/ or water ligands and/or lattice water molecules (calc. 12.13% for 2, 8.53% for 3 and 11.94% for 4). The second weight losses of 59.85% at 220-700 °C for 2, 63.09% at 260-750 °C for 3 and 59.67% at 230-750 °C for 4 are attributed to collapse of the frameworks (calc. 62.34% for 2, 67.42% for 3 and 63.29% for 4). The residual weights (28.51% for 2, 28.25% for 3 and 28.23% for 4) correlate with NiO (calcd 25.53% for 2, 24.05% for 3 and 24.77% for 4).

Photocatalytic activities

Organic dyes are harmful pollutants. Their high water solubilities make them difficult to degrade by conventional methods. Photocatalytic degradation is an effective method for the gradual decomposition of organic dyes into non-polluting organic acids and carbon dioxide. Insoluble homometallic nanoscale clusters can be effective photocatalysts for the degradation of organic complexes [25]. Therefore, we have tested complex **4** as a representative photocatalyst for the degradation of methyl orange (MO), methylene blue (MB) and rhodamine B (RhB) as model pollutants.

Under visible light irradiation, no significant degradation of MO could be observed upon adding complex **4** or without any catalyst (Fig. S3a, b). When the dye was MB, the degradation rate was increased from 25.2% (without any photocatalyst) to 31.6% after 180 min of photoirradiation. Hence, complex **4** exhibits a limited photocatalytic activity for the degradation of MB (Figs. 8a, b, 9). When the dye was RhB, the degradation rate of RhB increased from 14.6% (without any photocatalyst) to 15.8% after 180 min of photoirradiation, which is within the experimental error (Figs. S3c, d, S4).

XRPD tests showed that the pattern for complex **4** was unchanged after the photocatalytic experiment, indicating that the complex has good photocatalytic stability (Fig. S2).

Conclusion

In summary, the one-pot solvothermal system was used to prepare four different complexes of metal Ni(II) with **AMT**. Complex **4** shows limited photocatalytic selectivity for the degradation of some organic dyes.

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