

Syntheses, crystal structures and photocatalytic properties of transition metal complexes based on 9,10-anthraquinone-1,3-dicarboxylate

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Abstract

Five transition metal complexes based on the ligand 9,10-anthraquinone-1,3-dicarboxylate acid (1,3-H₂AQDC) have been synthesized and characterized by physico-chemical and spectroscopic methods. Single-crystal analyses show that the complexes {Mn(1,3-AQDC)(H₂O)₄·(H₂O)}_n, {Zn(1,3-AQDC)(H₂O)₄·(H₂O)}_n, {Ni(1,3-AQDC)(4,4'-bpy)(H₂O)₂(CH₃OH)}_n and {Co(1,3-AQDC)(4,4'-bpy)(H₂O)₂(CH₃OH)}_n (4,4'-bpy = 4,4'-bipyridine) comprise one-dimensional (1D) chains in their crystal structures, while [Ni(1,3-AQDC)(H₂O)₄·(H₂O)₃]₂ bears dimeric units, and these secondary building units are further linked by hydrogen bonding to form three-dimensional structures. These compounds proved to be able to catalyze visible-light-driven air-oxidation reactions of diarylethyne into diketones under mild conditions.

Introduction

The design and construction of functionalized coordination compounds has been one of the central themes in coordination chemistry, crystal engineering and supramolecular chemistry, ascribed to their established and/or potential applications in such fields as gas adsorption/separation, catalysis, sensors, molecular probes and magnetism [1–7]. Some general methods for functionalization of coordination complexes toward desired physical properties have been developed, such as wise selection of metal ions as nodes and/or organic ligands as linkers, rational design and synthesis of ligands/metal complexes, and post-synthetic modifications [8]. Carboxylate groups have very rich coordination modes that may result in diverse framework structures

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and have been widely used as coordination sites to fabricate novel metal–organic frameworks. Therefore, ligands with carboxylate groups are considered as excellent candidates for constructing versatile finite and infinite structures [9].

Quinones are good photosensitizers and play important roles in biological systems [10, 11], exhibiting rich redox properties in such processes as single electron transfer and proton-coupled electron transfer [12, 13]. In this study, the proligand 9,10-anthraquinone-1,3-dicarboxylic acid (1,3-H₂AQDC) has been synthesized, with the anthraquinone portion as photosensitizer to harvest light and carboxylate groups as coordination sites to bind metal ions. Five transition metal complexes based on this ligand have then been synthesized, which were characterized by single-crystal/powder X-ray diffraction, infrared spectra and thermal gravimetric analyses. Among them, the complexes $\{Mn(1,3-AQDC)(H_2O)_4 \cdot (H_2O)\}_n$ (1), $\{Zn(1,3-AQDC)(H_2O)\}_n$ AQDC)(H₂O)₄·(H₂O)₁ (2), {Ni(1,3-AQDC)(4,4'-bpy) $(H_2O)_2(CH_3OH)_1$ (4) and $\{Co(1,3-AQDC)(4,4'-bpy)\}$ $(H_2O)_2(CH_3OH)_n$ (5) (4,4'-bpy=4,4'-bipyridine) bear onedimensional (1D) chains in their crystal structures, while $[Ni(1,3-AQDC)(H_2O)_4 \cdot (H_2O)_3]_2$ (3) comprises dimeric units. Hydrogen bonding interactions exist widely in these complexes, which link the dimers/chains into three-dimensional frameworks.

Inspired by our recent studies on the photocatalytic activities of metal complexes derived from 9,10-anthraquinone-1,4-dicarboxylic acid [14], we investigated the photocatalytic properties of these complexes in promoting organic reactions. As an important category of organic molecules used for synthesizing biologically active heterocyclic compounds, 1,2-diketones have attracted lots of synthetic efforts utilizing different catalysts based on metal complexes comprising Pd [15, 16], Au [17], Ru [18, 19] and Cu [20], as well as the organic dye eosin Y [21]. Along this line, the air-oxidation reactions of alkynes to produce 1,2-diketones under the irradiation of visible light were selected as the template reaction to verify the photocatalytic activity of complexes **1–5**. They proved to be good heterogeneous catalysts, being able to catalyze visible-light-driven oxidation reactions of diphenylethyne into benzil in air under mild conditions, in different yields.

Experimental

Materials and methods

All reagents and solvents were obtained from commercial suppliers and used without further purification. The proligand 1,3-H₂AQDC was synthesized using a modified procedure as reported [22]. Thermal analyses were carried out under nitrogen flow on a Mettler-Toledo TGA/DSC STARe system in the temperature range of 25 to 800 °C with a heating rate of 10 °C min⁻¹. Elemental analyses were performed using a PE-240C elemental analyzer. Infrared spectra were recorded on a VECTOR 22 spectrometer with pressed KBr pellets in the range of 4000 to 400 cm⁻¹. ¹H and ¹³C NMR spectra were obtained in CDCl₃ on a Bruker 400 MHz spectrometer.

Synthesis of 9,10-anthraquinone-1,3-dicarboxylate acid

1,3-Dimethylanthraquinone (7.55 g, 32.0 mmol) was dissolved into a mixed solvent of pyridine (300 ml) and water (200 ml) and heated to reflux. Then, $KMnO_4$ (161.70 g, 125 mmol) was added gram by gram in 48 h. After being cooled to room temperature, the precipitated MnO₂ was filtered off. The filtrate was then subjected to rotary evaporation to yield a yellow oil, and the filtration bed was extracted with a 20% aqueous solution of KOH (5×100 ml). The basic extractions were combined together and concentrated to approximately one-third of their original volume with a rotary evaporator. This residue was then combined with the above-mentioned yellow oil, which was then acidified to pH = 1 with concentrated hydrochloric acid to precipitate a yellow powder. The yellow powder was collected by filtration and treated with diethyl ether. After being dried in air, pure 9,10-anthraquinone-1,3-dicarboxylate acid was obtained in 33% yield. ¹H NMR (400 MHz, d_6 -DMSO) δ (ppm) 13.72 (s, 2H), 8.69 (d, J = 2.0 Hz, 1H), 8.19 (m, 3H), 7.95 (m, 2H). *Anal*. Calcd for C₁₆H₈O₆: C, 64.87; H, 2.72. Found: C, 64.91; H, 2.70.

Synthesis of complex 1

{Mn(1,3-AQDC)(H₂O)₄·(H₂O)}_n (1): A mixture of Mn(OAc)₂·4H₂O (12.2 mg, 0.05 mmol) and 1,3-H₂AQDC (14.8 mg, 0.05 mmol) was dissolved into 5.0 mL water with stirring. The reaction solution was filtrated and allowed to evaporate at room temperature for 1 week to give yellow crystals, which were collected by filtration and washed with acetone (20.3 mg, yield: 46%). *Anal.* Calcd for $C_{16}H_{16}MnO_{11}$: C, 43.75; H, 3.67. Found: C, 43.58; H, 3.75. IR (KBr, cm⁻¹): 1670(s, C=O), 1580(s, carboxylate C=O), 1280(s, C=O).

Synthesis of complex 2

 ${Zn(1,3-AQDC)(H_2O)_4 \cdot (H_2O)}_n$ (2): This complex was obtained by the same procedure as that for 1 using Zn(OAc)_2·2H_2O instead of Mn(OAc)_2·4H_2O. Yellow needlelike crystals were obtained by filtration and washed with water and acetone (39.1 mg yield: 87%). *Anal.* Calcd for C₁₆H₁₆O₁₁Zn: C, 42.74; H, 3.59. Found: C, 43.01; H, 3.65. IR (KBr, cm⁻¹): 1670(s, C=O), 1590(s, carboxylate C=O), 1280(s, C–O).

Synthesis of complex 3

[Ni(1,3-AQDC)(H₂O)₄·(H₂O)₃]₂ (**3**): A mixture of Ni(OAc)₂·4H₂O (24.8 mg, 0.10 mmol) and 1,3-H₂AQDC (14.8 mg, 0.05 mmol) was dissolved into 5.0 mL water and stirred together. Filtration followed by acetone diffusion afforded green plate-like crystals in several days (36.4 mg, yield: 76%). *Anal.* Calcd for C₁₆H₂₀NiO₁₃: C, 40.12; H, 4.21. Found: C, 40.31; H, 4.17. IR (KBr, cm⁻¹) 1670(s, C=O) 1590(s, carboxylate C=O), 1280(s, C–O).

Synthesis of complex 4

{Ni(1,3-AQDC)(4,4'-bpy)(H₂O)₂(CH₃OH)}_n (**4**): A mixture of 1,3-H₂AQDC (14.8 mg, 0.05 mmol), Ni(OAc)₂·4H₂O (24.8 mg, 0.10 mmol) and a 1.0 mL methanol solution of 4,4'-bpy (15.6 mg, 0.10 mmol) was placed in a Parr Teflon-lined stainless steel vessel (25.0 mL) and heated to 120 °C for 3 days. Green crystals were obtained in 48 h on cooling to room temperature slowly, which were collected by filtration and washed with methanol (43.4 mg, yield: 87%). *Anal.* Calcd for C₂₂H₁₈NNiO₉: C, 52.95; H, 3.64; N, 2.81. Found: C, 52.80; H, 3.55; N, 2.99. IR (KBr, cm⁻¹): 1670(s, C=O), 1580(s, carboxylate C=O), 1420(s, C–N), 1280(s, C–O).

Synthesis of complex 5

 $\{Co(1,3-AQDC)(4,4'-bpy)(H_2O)_2(CH_3OH)\}_n$ (5): Compound 5 was obtained by the same procedure as that for 4 except that $Co(OAc)_2 \cdot 4H_2O$ was used instead of Ni(OAc)₂·4H₂O as starting material. Pink crystals were obtained by filtration and washed with methanol (26.4 mg, yield: 53%). Anal. Calcd for C₂₂H₁₈CoNO₉: C, 52.92; H, 3.63; N, 2.81. Found: C, 52.66; H, 3.84; N, 2.90. IR (KBr, cm⁻¹): 1668(s, C=O), 1579(s, carboxylate C=O), 1417(m, C-N). 1282(m. C-O).

Typical procedure for photocatalytic experiments

The photocatalyst (0.02 mmol), 1,2-diphenylethyne (35.6 mg, 0.2 mmol) and 4-chlorobenzenethiol (57.8 mg, 0.4 mmol) were mixed in 2.0 mL MeCN. The reaction mixture was stirred at room temperature under the irradiation of a blue LED for 84 h in ambient air. Filtration was done on completion of the reaction. The thus collected filtrate containing the final product was evaporated to dryness and subjected to column chromatography (silica gel, petroleum ether/ethyl acetate) to afford pure benzil as a yellow solid. The catalyst isolated by filtration was washed by dichloromethane and dried in air before being subjected to recycled use. ¹H NMR of benzil (400 MHz, CDCl₃) δ (ppm) 7.90 (d, J = 8.8 Hz, 4H), 7.60 (t, J = 7.4 Hz, 2H), 7.51 (t, J = 8.0),

 Table 1
 Crystallographic data for complexes 1–5

4H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 194.6, 134.9, 133.0, 129.9, 129.0,

X-ray crystallography

Single-crystal X-ray diffraction data of all five complexes were collected at 293 K on a Bruker APEX II CCD diffractometer operating at 50 kV and 30 mA using Mo Ka radiation ($\lambda = 0.71073$ Å). Data were integrated by SAINT and scaled with either a numerical or multi-scan absorption correction using SADABS [23]. All structures were solved by direct methods or Patterson maps [24] and refined by full-matrix least squares on F^2 using the SHELXL-2014 [25] and OLEX2 [26] programs. All non-hydrogen atoms were refined anisotropically. Non-water hydrogen atoms were added at calculated positions and refined using a riding model. Hydrogen atoms of water molecules were located by difference Fourier maps and refined using a riding model at restrained distance of 0.86 Å. Crystallographic data for all five complexes are summarized in Table 1.

Results and discussion

Crystal structures of complexes 1 and 2

Complexes $\{Mn(1,3-AQDC)(H_2O)_4 \cdot (H_2O)\}_n$ (1) and $\{Zn(1,3-AQDC)(H_2O)_4 \cdot (H_2O)\}_n$ (2) are isostructural,

	1	2	3	4	5
Empirical formula	C ₁₆ H ₁₆ MnO ₁₁	C ₁₆ H ₁₆ O ₁₁ Zn	C ₁₆ H ₂₀ NiO ₁₃	C ₂₂ H ₁₈ NNiO ₉	C ₂₂ H ₁₈ NCoO ₉
Fw	439.23	449.66	479.03	499.08	499.30
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	ΡĪ	$P2_1/n$	$P2_1/c$	$P2_1/c$
<i>a</i> (Å)	9.583(5)	9.6470(19)	7.2689(4)	10.7127(18)	10.770(8)
<i>b</i> (Å)	9.851(5)	9.7839(19)	24.5673(12)	15.200(3)	15.222(12)
<i>c</i> (Å)	10.187(5)	10.110(2)	10.7500(5)	12.976(2)	12.995(10)
α (°)	116.985(11)	117.171(2)	90	90	90
β (°)	97.827(8)	98.057(2)	90.350(3)	106.545(2)	106.953(11)
γ (°)	92.689(7)	92.512(2)	90	90	90
$V(\text{\AA})$	842.5(7)	834.3(3)	1919.67(17)	2025.4(6)	2038(3)
Ζ	2	2	4	4	4
$D_c (g \cdot cm^{-3})$	1.731	1.790	1.657	1.637	1.627
$\mu (\mathrm{mm}^{-1})$	0.848	1.537	1.081	1.106	0.900
F(000)	450	460	992	1028	1024
$R_{I}^{a}, w R_{2}^{b} [I > 2\sigma (I)]$	0.0295, 0.0841	0.0283, 0.0866	0.0327, 0.0630	0.0369, 0.0975	0.0525, 0.1074
$R_1^{\rm a}$, $wR_2^{\rm b}$ (all data)	0.0325, 0.0867	0.0337, 0.0908	0.0549, 0.0714	0.0431, 0.1016	0.0963, 0.1285
$(\Delta \rho) \max, (\Delta \rho) \min (e \text{ Å}^{-3})$	0.385/- 0.367	0.35/- 0.26	0.33/- 0.52	0.48/- 0.87	0.89/- 0.90

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ^b $wR_2 = \left\{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \right\}^{1/2}$

both crystallize in triclinic space group $P\overline{1}$. One metal atom, which is Mn(II) in 1 and Zn(II) in 2, one 1,3-AQDC²⁻ ligand, four water ligands and one lattice water molecule constitute the asymmetric unit in the crystal structure. The metal centers adopt octahedral geometry composed of two carboxylate oxygen atoms from two symmetry-related ligands and four water ligands (Fig. 1 with compound 2 as example). The Mn–O bond distances in complex 1 are between 2.136(2) and 2.209(2) Å, while the Zn–O bond lengths in compound 2 fall in the range of 2.052(2)-2.167(7) Å. The dihedral angles between the carboxylate groups (1- and 3-positions) and the attached phenyl rings are $69.3(1)^{\circ}$ and $18.2(1)^{\circ}$ for **1**, and $69.5(1)^{\circ}$ and $17.4(1)^{\circ}$ for 2, respectively, indicating the most constrained ligand conformation in this family of metal complexes. The μ_2 -briding 1,3-AQDC²⁻ ligands connect the six-coordinated metal centers into 1D chains, which further assemble into a 3D network via intermolecular hydrogen bonding (Table 2).

Crystal structure of complex 3

Single-crystal X-ray diffraction reveals that [Ni(1,3-AQDC)(H₂O)₄·(H₂O)₃]₂ (**3**) crystalizes in monoclinic space group $P2_1/n$. The asymmetric unit of **3** contains one Ni(II) atom, one 1,3-AQDC²⁻ anion, four water ligands and two lattice water molecules. The distorted octahedron configuration of the Ni(II) center is constituted by oxygen atoms from four water ligands and two carboxylate groups of two symmetry-related 1,3-AQDC²⁻ ligands. The Ni-O bond contacts range from 2.025(2) to 2.097(2) Å. The dihedral angles between the carboxylate groups and their attached phenyl rings are 98.5(1)° and 28.5(1)° for the 1- and 3-positions, respectively. The 1,3-AQDC²⁻ ligands take μ_2 -briding mode to form dimeric moieties that are further stabilized by intramolecular hydrogen bonding (Fig. 2). Very rich intermolecular hydrogen bonding motifs also exist in the crystal packing of compound 3, contributing to the assembly of the dimers into a 3D supramolecular structure (Table 2).

Crystal structures of complexes 4 and 5

Complexes { $Ni(1,3-AQDC)(4,4'-bpy)(H_2O)_2(CH_3OH)$ }_n (4) and $\{Co(1,3-AQDC)(4,4'-bpy)(H_2O)_2(CH_3OH)\}_n$ (5) are isostructural, both crystallizing in monoclinic space group $P2_1/c$. In their crystal structures, each asymmetric unit contains one divalent metal atom, one 1,3-AQDC²⁻ ligand, half a 4,4'-bpy ligand, one methanol ligand and two water ligands. The metal center is six-coordinated by two carboxylate O atoms from two symmetry-related 1,3-AQDC²⁻ ligands, one N atom from 4,4'-bpy, and three O atoms from coordinated methanol and water ligands (Fig. 3a with 4 as the example). The 1- and 3-positioned carboxylate groups of the ligand also hold different dihedral angles to the attached phenyl ring, being $84.4(1)^\circ$ and $11.4(1)^\circ$ for 4, and $83.1(1)^{\circ}$ and $11.0(1)^{\circ}$ for 5, respectively. In 4, the Ni–O/N bond lengths fall in the range of 2.033(2)-2.103(2) Å and the nonlinear O-Ni-O/N bond angles are between 83.15(7) and $93.96(7)^{\circ}$. These parameters in 5 are comparable with those in 4, with the Co-O/N bond distances ranging from 2.042(3) to 2.155(4) Å and the nonlinear O-Co-O/N bond angles between 82.99(13)° and 94.75(13)°. It is interesting that these complexes also bear dimeric units similar as that in compound 3, which are linked by the auxiliary ligands 4,4'-bpy to form 1D stair-like chains (Fig. 3b with 4 as the example). The 1D chains are interconnected by hydrogen bonding interactions to form a 3D structure (Table 2).

Structural comparison and solubility

Compared to previously reported metal complexes based on the isomeric ligand 9,10-anthraquinone-1,4-dicarboxylate acid (1,4-AQDC), complexes of 1,3-AQDC exhibit lower dimensionalities (0D and 1D for complexes of 1,3-AQDC v.s. 1D, 2D and 3D for complexes of 1,4-AQDC). This might be related to the structural differences of the ligand associated with their intrinsic restraint generated from steric hindrance between the carboxylate groups and adjacent





 Table 2
 Hydrogen bonding parameters in complexes 1-5 (Å and deg)

Complex	D-H A	$D(H^{\dots}A)$	$D(D^{\dots}A)$	∠DHA
1	O7 W-H7 WA O5 ⁱ	2.04	2.864(2)	162.8
	O7W-H7WB O3 ⁱⁱ	2.06	2.814(2)	145.7
	O8 W-H8 WA O6 ⁱⁱⁱ	1.87	2.713(2)	170.7
	O8W-H8WB O4 ^{iv}	2.11	2.830(2)	142.3
	O9 W-H9WAO11 W	1.89	2.721(2)	164.0
	O9 W-H9WBO6	2.00	2.718(2)	141.5
	O10 W-H10A O1 ⁱ	1.90	2.750(2)	170.4
	O10 W-H10B ··· O4 iii	2.06	2.855(2)	156.6
	O11 W-H11BO4 ⁱⁱⁱ	2.01	2.848(2)	169.5
Symmetry $1 - y, -x$	codes: ${}^{i}1 - x, 2 - y, 1 - z; {}^{i}z; {}^{iv} + x, 1 + y, + z$	$x^{ii}1 - x, 1 - y$, 1−z; ⁱⁱⁱ 1−	·x,
2	O7 W-H7WA…O11 W	1.88	2.722(3)	164.7
	O7 W-H7WB O4	1.93	2.677(3)	144.6
	O8 W-H8 WA O4 ⁱ	1.90	2.729(3)	162.5
	O8W-H8WB O6 ⁱⁱ	2.04	2.775(3)	143.6
	O9 W-H9 WA O3 ⁱⁱⁱ	2.04	2.875(3)	163.4
	O9W-H9WBO5iv	2.13	2.829(3)	138.3
	O10 W-H10AO6i	2.11	2.902(3)	152.8
	O10 W-H10BO2 ⁱⁱⁱ	1.93	2.765(3)	163.1
	O11 W-H11BO6 ⁱ	2.03	2.859(3)	162.1
Symmetry $1-z$; ^{iv} 1	codes: ${}^{i}1-x$, $1-y$, $2-z$; ${}^{i}-x$, $1-y$, $1-z$.	$x^{ii} + x, -1 + x^{ii}$	y, +z; ⁱⁱⁱ 1 –	х, <i>—</i> у,
3	O7 W-H7 WA O2 ⁱ	1.94	2.788(2)	168.1
	O7W-H7WB O5 ⁱⁱ	1.82	2.670(2)	170.3
	O8 W-H8WA O12 W	1.94	2.771(2)	163.0
	O8 W-H8WB…O11W ⁱⁱⁱ	1.91	2.751(2)	166.2
	O9 W-H9 WA…O5	1.86	2.693(2)	163.2
	O9W-H9WB O3 ^{iv}	1.81	2.630(2)	159.5
	O10 W-H10AO12W ^v	1.93	2.791(2)	177.1
	O10 W-H10BO13Wvi	1.97	2.828(3)	175.4
	O11 W-H11AO3	1.91	2.712(2)	155.2
	O11 W-H11BO13vii	1.93	2.763(3)	161.4
	O12 W-H12A…O1viii	2.09	2.875(2)	151.2
	O12 W-H12BO11Wiv	1.97	2.825(3)	171.9
	O13 W-H13AO9 W	1.91	2.754(2)	167.7
Symmetry 1/2 + y, 1 $v^{i}1/2 + x$, 3/2 - y, -	codes: ${}^{i}1-x$, $1-y$, $1-z$, ${}^{i}1/2-z$, ${}^{iv}1-x$, $1-y$, $-z$, v , ${}^{3}/2-y$, ${}^{1}/2+z$, ${}^{vii}1/2-x$, ${}^{-1}/2+z$	$x^{ii}1 + x, +y, -1/2 + x, 3$ - 1/2 + y, 1/2	+z; ⁱⁱⁱ 3/2 – x /2 – y, 1/2 + 2 – z; ^{viii} 1/2 ·	, z; +x,
4	O7-H7A O5 ⁱ	1.86	2.666(3)	151.4
	O8 W-H8 WA O1 ⁱⁱ	2.22	2.833(3)	128.3
	O8 W-H8WA O5 ⁱⁱ	2.20	2.861(3)	133.7
	O8W-H8WB O2 ⁱⁱⁱ	2.03	2.865(3)	162.6
	O9 W-H9 WA O5 ⁱⁱ	1.91	2.746(3)	162.3
	O9W-H9WB O3	1.83	2.646(3)	156.9

carbonyl groups. Regarding the dihedral angles of carboxylate groups with attached phenyl rings, those for the 3-positioned ones in 1,3-AQDC are much smaller than the other ones in complexes of both 1,3-AQDC and 1,4-AQDC.

Table 2 (continued)					
Complex	D-H A	D(H···A)	D(D···A)	∠DHA	
Symmetry codes: ${}^{i}1-x$, $1-y$, $1-z$; ${}^{ii}1-x$, $-1/2+y$, $3/2-z$; ${}^{iii}1+x$, $+y$, $+z$					
5	O8 W-H8 WA O3	1.83	2.668(4)	164.6	
	O8W-H8WB O6 ⁱ	1.90	2.748(5)	167.9	
	O9 W-H9 WA […] O2 ⁱⁱ	2.00	2.854(5)	175.0	
	O9 W-H9WB O1 ⁱ	2.20	2.829(5)	129.4	
	O9W-H9WB O6 ⁱ	2.15	2.864(4)	140.4	
	O7-H7 O6 ⁱⁱⁱ	1.93	2.670(5)	154.0	
Symmetry	codes: $^{i}1 - x$, $1/2 + y$, $3/2 - y$	- z; ⁱⁱ 1 + x, +	+x, +z; iii1 -	- x,	
1 - V, $1 - Z$					



Fig. 2 The dimeric unit in complex **3** showing coordination geometry of Ni(II) center and binding mode of 1,3-AQDC^{2–} ligand. Symmetry codes: ${}^{i}-x+1, -y+1, -z+1$

Conjugation of the 3-positioned carboxylate group with an attached phenyl ring makes it less favorable for higher connectivity at this site and thus resulted in different binding modes of the ligand 1,3-AQDC as compared to 1,4-AQDC, leading to metal complexes of different dimensionalities.

Complexes 1-5 are all slightly soluble in DMSO but not soluble in water and other common organic solvents including methanol, DMF, acetonitrile, acetone, tetrahydrofuran and dichloromethane. It is interesting that complex **3** with discrete dimeric structural units exhibits similar poor solubility as that of the coordination polymers in this family, which might be ascribed to very rich hydrogen bonding interactions in its crystal packing.

Thermogravimetric analyses

Thermal analyses for complexes 1-5 were performed from 25 to 800 °C under a nitrogen atmosphere at a heating rate



Fig.3 a Coordination geometry of Ni(II) center and binding mode of ligand in complex 4; b 1D chain structure in complex 4. Symmetry codes: $i^{i}-x+1, -y+1, -z+1$



Fig. 4 TGA curves for complexes 1–5

of 10 °C min⁻¹ (Fig. 4). All water molecules (including the coordinated and lattice ones) of compound **1** were lost between 68 and 149 °C (obsd 21.54%, calcd 20.50%). However, the solvent molecules in crystalline samples of complexes **2** and **3** are not stable at room temperature, resulting in weight loss before heating, which makes it hard to correlate the weight loss percentage with the loss of coordinated or lattice solvents. It is interesting that the coordinated solvent molecules in **4** are gone between 121 and 180 °C (obsd 12.52%, calcd 13.62%), while those in **5** are gone between 83 and 117 °C (obsd 12.11%, calcd 13.62%), although the two complexes are isostructural. Further decomposition temperatures are 300 °C for compound **4** and 312 °C for **5**.

Photocatalytic activity

In our recent studies of the photocatalytic activities of metal complexes based on 9,10-anthraquinone-1,4-dicarboxylate [14], we have demonstrated that these kinds of anthraquinone-functionalized coordination complexes are able to catalyze the visible-light-driven air-oxidation reactions of diarylalkynes into 1,2-diketones under mild conditions.

 Table 3
 Studies of the catalytic performance of the complexes

	photocatalyst 4-chlorobenzenethiol blue LED, air, 84h CH ₃ CN	
Entry	Photocatalyst (mol %)	Yield (%)
1	Complex 1 (10)	47
2	Complex 2 (10)	58
3	Complex 3 (10)	71
4	Complex 4 (10)	49
5	Complex 5 (10)	33
6	Complex 3 (10) (in the dark)	0
7	Complex 3 (10) (without 4-chlorobenzenethiol)	Trace
8	_	0
9	Complex 3 (10) (under 1 atm N_2 atmosphere)	0

Therefore, we investigated the photocatalytic activity of these complexes based on 9,10-anthraquinone-1,3-dicarboxylate. We found that these complexes are able to promote the air-oxidation of diarylethyne into diketones at ambient conditions when irradiated by a blue LED. These heterogeneous catalysts hold the advantages of easy isolation and recycling as compared to conventional homogeneous photocatalysts such as complexes with precious metals and organic dyes [15–21].

All of the complexes were subjected to the evaluation of catalytic activities for promoting the above-mentioned photooxidation reaction of 1,2-diphenylethyne into benzil (Entries 1–5 in Table 3). The results reveal that they all exhibit moderate activities except complex **5**. However, the catalytic activities of these complexes are not as good as our previously reported Ni(II) complex [14], which gives 81% isolated yield on this substrate. For further comparison, Ni(II) complex **3** showing the best efficiency was used as the catalyst for a few other substrates under the same reaction conditions, as shown in Table **4**. These reactions further demonstrate that complex **3** is less efficient in catalyzing these photo-oxidation reactions





as compared to our previous reported Ni(II) complex. Experimental observations suggest that the reaction mechanism should be the same as the one reported in our previous study, because further studies revealed that no reaction was observed in the absence of the factors of photocatalyst, 4-chlorobenzenethiol, blue LED and air (entry 6–9 in Table 3) [14].

These complexes are easily isolated from the reaction mixture by filtration, and could be recycled in catalyzing the photo-oxidation reaction with no obvious loss of activity. In the case that 3 was recycled for further catalysis with 1,2-diphenylethyne as substrate, benzil could be obtained in 63-67% yields for three cycles. Only trace amounts of metal ions were detected in the filtrate obtained after the reaction using ICP analysis, indicating less than 0.01% catalyst loss for all complexes. As has been proposed in the description of solubility, very rich hydrogen bonding interactions in complex 3 decrease its solubility significantly to the same level as that for other coordination polymers in this series, which also accounts for the same level of metal leaching after catalysis. The recyclability of Ni(II) complexes in this work is about the same as that of the Ni(II) complex previously reported, but the catalytic efficiency is not as good as the previously reported one. A plausible explanation is that steric hindrance between carboxylate groups and adjacent carbonyl groups is different in 1,3- and 1,4-anthraquinone dicarboxylate, resulting in different conjugation systems in the ligands and distinct electronic properties regarding coordination, which subsequently affects catalytic properties of their metal complexes.

Conclusion

In summary, a new functionalized ligand, 9,10-anthraquinone-1,3-dicarboxylate acid, has been synthesized. Five transition metal complexes have been synthesized subsequently, and their crystal structures have been investigated. The metal centers of all of these complexes have aqua ligands in their coordination spheres and form onedimensional chains or dimeric units through the connections of the anionic ligand, which are further linked by versatile hydrogen bonding motifs to generate three-dimensional networks. These metal complexes could be used as heterogeneous photocatalyst for the photo-oxidation of diarylalkynes into 1,2-diketones. Current research is focused on exploration of new reaction systems in which these complexes could be used as more efficient heterogeneous photocatalysts.

Supplementary materials

CCDC 1870373 and 1832026-1832029 contain the supplementary crystallographic data for complexes **1–5**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_reque st/cif.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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