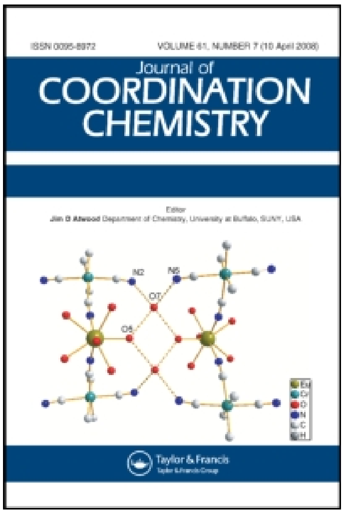

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Synthesis, characterization and antimicrobial activity of five metal complexes of <i>N</i>-acetyl-9-hydroxyl-fluorene-9-hydrazide

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Synthesis, characterization and antimicrobial activity of five metal complexes of *N*-acetyl-9-hydroxyl-fluorene-9-hydrazide

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Five mononuclear metal (Mn, Co, Ni, Cu, Zn) complexes have been prepared using a monoanionic tridentate ligand *N*-acetyl-9-hydroxyl-fluorene-9-hydrazidate (ahfhz$^-$) and characterized by elemental analysis, ESI-MS, IR, UV, ^{1}H NMR and ^{13}C NMR. Antibacterial screening data showed that the cobalt and copper complexes and Hahfhz have moderate antimicrobial activity. The five metal complexes have some antagonistic effect against the ligand to Gram$^+$ bacteria *Staphylococcus aureus* and *Bacillus subtilis*. The decrease in the efficiency of metal complexes may be assigned to the zero charge of the central core. $[Co(ahfhz)_2]\cdot 2CH_3OH$ (**3**) crystallizes in monoclinic system with space group $P2_1/n$, $a = 13.1379(7)$ Å, $b = 17.7809(10)$ Å, $c = 14.7403(8)$ Å, $\beta = 110.0580(10)^\circ$; in the crystal structure packing N–H$\cdots$O, O–H$\cdots$O and C–H$\cdots\pi$ hydrogen bonding interactions lead to a supramolecular structure.

Keywords: Metal complexes; *N*-acetyl-9-hydroxyl-fluorene-9-hydrazide; Crystal structure; Antimicrobial activity

1. Introduction

In 1960 some interesting effects of fluorene-9-carboxylic acids on plants were observed and 9-hydroxy-fluorene-9-carboxylic acid and its derivatives are considered as new multifunctional plant-growth regulators [1, 2]. The 9-hydroxy-fluorene-9-carboxylic acid has two potentially coordinating oxygen atoms from hydroxyl and carboxyl, similar to salicylic acid [3]. Mononuclear and binuclear complexes of 9-hydroxy-fluorene-9-carboxylic acid with copper ions [4, 5], 1-D chain cadmium coordination polymer [6] and hexanuclear organostannoxane cage supramolecular structures have been reported [7].

N-acylhydrazides, as pentadentate constructing ligands, have received special attention due to ease of formation of metal clusters with metal ions such as Ga^{3+}, Co^{3+}, Fe^{3+}, Mn^{3+} and Ni^{2+} [8–11]. In our previous studies to examine the mode of binding and possible antagonistic effects for hydrazide, antibacterial screening data showed that the complexes formed with alike or synergistic ligands are more active than the simple metallic salts or carboxylate complexes [12, 13]. Thus, our interest focused on fluorenylhydrazides (figure 1) and transition metals.

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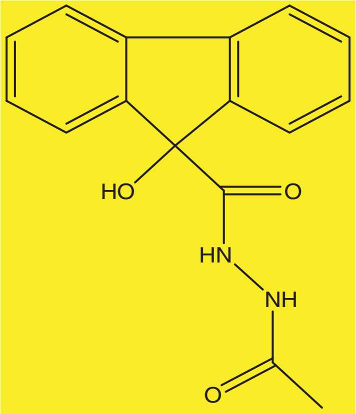


Figure 1. Hahfhz.

In the present article, we report a new potentially tridentate ligand, *N*-acetyl-9-hydroxyl-fluorene-9-hydrazide (**1**) (Hahfhz), and five metal complexes. The deprotonated *N*-acetyl-9-hydroxyl-fluorene-9-hydrazidate (ahfhz$^-$) may bridge the central ion through its hydroxyl, hydrazide *N* atom and acetyl group. The existence of intermolecular hydrogen bonds and C–H $\cdots \pi$ interactions may make the complexes more stable. Minimum inhibitory concentrations (MIC) of the complexes against four different bacteria were also measured.

2. Experimental

2.1. *Materials*

Chemicals for the synthesis of the compounds were used as purchased. Methanol and ethanol were used without any further purification. Phenanthraquinone, sulfuric acid, hydrazine hydrate, acetic anhydride, diethyl ether, sodium hydrate, $MnAc_2 \cdot 4H_2O$, $CoAc_2 \cdot 4H_2O$, $NiAc_2 \cdot 4H_2O$, $CuAc_2 \cdot H_2O$ and $ZnAc_2 \cdot 2H_2O$ were purchased from China Sinopharm Group Chemical Reagent Co., Ltd., Wuhan, China. All chemicals and solvents were reagent grade. The *Staphylococcus aureus*, *Escherichia coli*, *Bacillus subtilis* and *Proteus vulgaris* were purchased from China Center for Type Culture Collection.

2.2. *Physical measurements*

Infrared spectra were measured on a Thermo Nicolet Corporation NEXUS FT-IR spectrometer as KBr pellets in the 4000–400 cm^{-1} region. UV-Vis spectra were recorded on a Shimadzu-UV-2501 PC recording spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Inova 600 MHz NMR spectrometer at 25°C. Chemical shifts were referenced to residual solvent. C, H and N elemental analysis were performed on a Perkin-Elmer 2400 CHN elemental analytical instrument; Mn, Co, Ni, Cu and Zn were determined by atomic absorption spectroscopy on a Perkin-Elmer 1100B spectrophotometer. Positive and negative electrospray ionization mass spectra (ESI-MS) were performed on an API-2000 LC/MS/MS system for the complex in methanol.

2.3. *Synthesis of the ligand and complexes*

2.3.1. Synthesis of Hahfhz (1). A mixture of 9-hydroxyl-fluorene-9-hydrazide (1.0 g, 4.2 mmol) and acetic anhydride (20 mL) was stirred for 1 h at room temperature, then warmed slowly to 40°C and stirred for 4 h. After the reaction was finished, the reaction mixture was cooled and then quenched by the addition of 20 mL water (the excess acetic anhydride was hydrolyzed to acetic acid), filtered and rinsed with water and diethyl ether. The filtrate was kept at room temperature overnight, and the solvent was removed in a vacuum drying oven. Yield: 0.95 g, 80.9%. M.p.: 206–208°C. Found: C, 68.23; H, 5.24; N, 9.76%. Calcd for $C_{16}H_{14}N_2O_3$: C, 68.06; H, 5.01; N, 9.92%. IR (KBr pellet, cm^{-1}): 3386 (s); 3333 (vs); 3213 (s); 3023 (s, b); 1691 (m); 1648 (vs); 1537 (m); 1481 (m); 1450 (m); 1374 (m); 1282 (m); 1228 (m); 1209 (m); 1107 (m); 1070 (m); 770 (m); 748 (m); 732 (m). ^1H NMR (DMSO), δ ppm: 10.00 (s, 1H, Fluo–CO–NH–); 9.87 (s, 1H, Me–CO–NH–); 7.77 (m, 2H, 4-, 5-FluoH); 7.47 (m, 2H, 1-, 8-FluoH); 7.40 (m, 2H, 3-, 6-FluoH); 7.31 (m, 2H, 2-, 7-FluoH); 1.84 (s, 3H, $-CH_3$). ^{13}C NMR (DMSO), δ ppm: 170.91 (Fluo–CO–); 168.57 (Me–CO–); 147.95 (4a-FluoC, 4b-FluoC); 141.06 (8a-FluoC, 9a-FluoC); 129.76 (1-FluoC, 8-FluoC); 128.43 (4-FluoC, 5-FluoC); 124.81 (3-FluoC, 6-FluoC); 120.73 (2-FluoC, 7-FluoC); 83.83 (9-FluoC); 21.20 ($-CH_3$). UV-Vis (10^{-4} mol L^{-1} in methanol), λ_{max} (nm): 274, 307.

2.3.2. Synthesis of [Mn(ahfhz)$_2$]·4CH$_3$OH (2). *N*-acetyl-9-hydroxyl-fluorene-9-hydrazide (0.56 g, 2.0 mmol) was dissolved in 100 mL methanol. Methanol solution containing 0.25 g (1.0 mmol) $MnAc_2 \cdot 4H_2O$ was added dropwise to the above solution with stirring, followed by adjustment of pH to 5 with 1 wt% NaOH solution. The mixture was stirred for 2 h at room temperature. The lilac precipitate obtained was washed with methanol and dried over tissue article in air. Yield (based on Hahfhz): 65.5%, m.p.: >300°C. Found: C, 57.68; H, 5.56; N, 7.68; Mn, 7.56%. Calcd for $C_{36}H_{42}MnN_4O_{10}$: C, 57.98; H, 5.69; N, 7.52; Mn, 7.37%. IR (KBr pellet, cm^{-1}): 3392 (m); 3177 (vs, b); 1651 (vs); 1557 (vs); 1483 (m); 1399 (vs); 1290 (s); 1209 (s); 1108 (s); 1052 (s); 1020 (s); 771 (s); 750 (vs); 729 (vs); 620 (m); 556 (m). UV-Vis (10^{-4} mol L^{-1} in methanol), λ_{max} (nm): 273, 307.

2.3.3. Synthesis of [Co(ahfhz)$_2$]·2CH$_3$OH (3). **1** (0.56 g, 2.0 mmol) was dissolved in 100 mL methanol. Methanol solution containing 0.25 g (1.0 mmol) $CoAc_2 \cdot 4H_2O$ was added dropwise to the above solution with stirring, followed by adjustment of pH to 6 with 1 wt% NaOH solution. The mixture was stirred for 4 h at room temperature and filtered. Green plate crystals of $[Co(ahfhz)_2] \cdot 2CH_3OH$ formed from the solution after 2 weeks. Yield: 62.0%, m.p.: >300°C. Found: C, 59.36; H, 5.04; N, 8.37; Co, 8.78%. Calcd for $C_{34}H_{34}CoN_4O_8$: C, 59.56; H, 5.01; N, 8.17; Co, 8.60%. IR (KBr pellet, cm^{-1}): 3636 (m); 3209 (vs, b); 1645 (vs); 1554 (vs); 1525 (vs); 1448 (vs); 1392 (vs); 1288 (s); 1204 (s); 1101 (s); 1081 (s); 1040 (vs); 1027 (vs); 771 (s); 749 (vs); 732 (vs); 607 (s); 501 (m). UV-Vis (10^{-4} mol L^{-1} in methanol), λ_{max} (nm): 267, 307, 680.

2.3.4. Synthesis of [Ni(ahfhz)$_2$]·2CH$_3$OH (4). **1** (0.56 g, 2.0 mmol) was dissolved in 100 mL methanol to which 10 mL of methanol solution containing 0.25 g (1.0 mmol) $NiAc_2 \cdot 4H_2O$ was added, followed by adjustment of pH to 6 with 1 wt% NaOH solution. This reaction mixture was magnetically stirred for 3 h. On filtration, a light-green precipitate was obtained. It was washed with methanol and dried over tissue article in air. Yield: 69.8%, m.p.: >300°C. Found: C, 59.38; H, 4.84; N, 8.00; Ni, 8.80%. Calcd for $C_{34}H_{34}NiN_4O_8$: C, 59.58; H, 5.01; N, 8.18; Ni, 8.56%. IR (KBr pellet, cm^{-1}): 3400 (m); 3320 (vs, b); 1648 (vs); 1541 (vs); 1479 (m); 1451 (s); 1401 (vs); 1209 (s); 1071 (s); 1043 (vs); 1003 (m); 775 (s); 747 (vs); 734 (vs); 622 (s); 560 (m). UV-Vis (10^{-4} mol L^{-1} in methanol), λ_{max} (nm): 271, 307, 650, 720.

2.3.5. Synthesis of [Cu(ahfhz)$_2$]·CH$_3$OH (5). **1** (0.56 g, 2.0 mmol) was mixed with 100 mL of methanol. Into this solution, 10 mL methanol solution containing 0.20 g (1.0 mmol) $CuAc_2 \cdot H_2O$ was added dropwise, followed by adjustment of pH to 4 with 1 wt% NaOH solution. The mixture was stirred for 3 h at room temperature. The green precipitate obtained was suction-filtered, washed several times with methanol and dried over tissue article. Yield: 78.6%, m.p.: >300°C. Found: C, 60.02; H, 4.49; N, 8.20; Cu, 9.71%. Calcd for $C_{33}H_{30}CuN_4O_7$: C, 60.22; H, 4.60; N, 8.51; Cu, 9.66%. IR (KBr pellet, cm^{-1}): 3434 (m); 3137 (vs, b); 1653 (vs); 1553 (vs); 1497 (vs); 1402 (vs); 1202 (m); 1104 (s); 1085 (s); 1040 (vs); 1026 (s); 765 (s); 752 (m); 729 (m); 622 (m); 560 (m). UV-Vis (10^{-4} mol L^{-1} in methanol), λ_{max} (nm): 270, 307, 659.

2.3.6. Synthesis of [Zn(ahfhz)$_2$]·2CH$_3$OH (6). **1** (0.56 g, 2.0 mmol) was mixed with 100 mL of methanol. Into this mixture, 10 mL of methanol solution containing 0.22 g (1.0 mmol) $ZnAc_2 \cdot 2H_2O$ was added dropwise, followed by adjustment of pH to 5 with 1 wt% NaOH solution. The mixture was stirred for 3 h at room temperature and filtered off. The yellow precipitate was washed with methanol to remove excess ligand and dried over tissue article in air. Yield: 73.2%, m.p.: >300°C. Found: C, 58.90; H, 4.83; N, 8.02; Zn, 9.56%. Calcd for $C_{34}H_{34}ZnN_4O_8$: C, 59.01; H, 4.96; N, 8.10; Zn, 9.45%. IR (KBr pellet, cm^{-1}): 3443 (m); 3141 (vs, b); 1662 (vs); 1606 (s); 1540 (s); 1498 (s); 1399 (vs); 1205 (s); 1087 (s); 1052 (m); 1020 (m); 771 (s); 752 (m); 622 (m); 558 (m). UV-Vis (10^{-4} mol L^{-1} in methanol), λ_{max} (nm): 268, 307.

2.4. *Antimicrobial activity*

The antimicrobial activity of the complexes was assessed by their ability to inhibit the growth of *S. aureus*, *E. coli*, *B. subtilis* and *P. vulgaris* in Mueller–Hinton broth medium. The Minimum Inhibitory Concentrations in $\mu g\, mL^{-1}$ against the four bacteria species were measured. Bacteria concentration was 5000–8000 cfu mL^{-1} and concentrations of 1600, 800, 400, 200, 100, 50, 25 $\mu g\, mL^{-1}$ of the complexes in methanol were tested. The solvent showed no antimicrobial action.

2.5. *X-ray crystal structure determination*

A crystal of **3** with dimensions of $0.20 \times 0.20 \times 0.06\ mm^3$ was selected. Intensity data were collected with a graphite monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å) at

292(2) K on a Bruker Smart APEX diffractometer. From a total of 25653 reflections in the $1.79 \le \theta \le 26.00°$ range, 6368 were independent with $R_{\text{int}} = 0.0625$, of which 4844 observed reflections with $I > 2\sigma(I)$ were used in the structural analysis. The structure was solved by Patterson methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed in calculated positions and/or in the positions from difference Fourier map. The positions and anisotropic thermal parameters of all non-hydrogen atoms were refined on F^2 by full-matrix least-squares with SHELXTL [14, 15]. The final refinement converged at $R_1 = 0.0424$, $wR_2 = 0.1043$ ($w = 1/[\sigma^2(F_o{}^2) + (0.0598P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$) (for 6368 unique reflections), $(\Delta/\sigma)_{\max} = 0.002$, $S = 0.954$, $(\Delta\rho)_{\max} = 0.328$ and $(\Delta\rho)_{\min} = -0.309\,\text{e}\,\text{Å}^{-3}$. The crystallographic data are given in table 1.

3. Results and discussion

3.1. *Synthesis of the complexes*

The metal complexes were synthesized from metal acetates and deprotonated *N*-acetyl-9-hydroxyl-fluorene-9-hydrazidate (ahfhz$^-$) in methanol (scheme 1). In the mixture, the *N*-acetyl-9-hydroxyl-fluorene-9-hydrazidate (ahfhz$^-$) can be obtained by adjustment of pH to about 5 with 1 wt% NaOH solution.

3.2. *Spectral characterization*

In the IR spectra of **1**, stretching bands at 1691 and 1648 cm^{-1} are attributed to C=O, at 1228, 1209, 1107 and 1070 cm^{-1} to C–OH (aromatic) and C–C (aromatic) and at

Table 1. Crystallographic data.

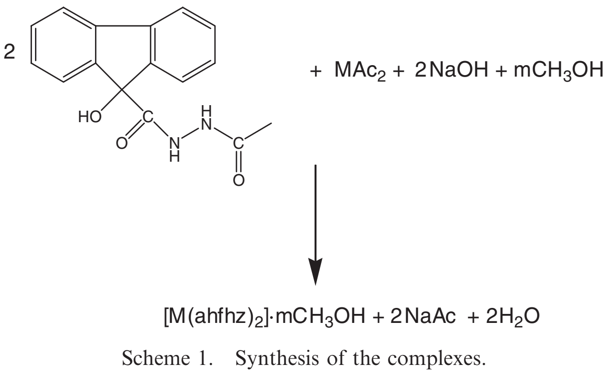
Empirical formula	$C_{34}H_{34}CoN_4O_8$
Formula weight	685.58
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	13.1379(7)
b (Å)	17.7809(10)
c (Å)	14.7403(8)
β (°)	110.0580(10)
V (Å^3)	3234.5(3)
Z	4
D_{Calcd} (Mg m^{-3})	1.408
μ (mm^{-1})	0.589
F(000)	1428
Crystal size (mm^3)	0.20 × 0.20 × 0.06
θ range (°)	1.79–26.00
Index ranges	$-16 \le h \le 16$ $-21 \le k \le 21$ $-18 \le l \le 17$
Observed reflections	25653
Independent reflections	6368 [$R_{\text{int}} = 0.0625$]
R_1	0.0424
wR_2	0.1043
Goodness-of-fit	0.954

3213 cm^{-1} to N–H [16, 17]. Bands at 3386 and 3333 cm^{-1} are assigned to υ(O–H) vibrations which may involve intramolecular and/or intermolecular hydrogen bonds [18, 19]. The medium intense band at 1481 cm^{-1} is attributed to δ(N–H) vibrations. The skeleton C=C vibration of the aromatic ring appears at 1450 cm^{-1}. Bands at 1374 and 1282 cm^{-1} are attributed to C–H and O–H deformation vibrations. The strong intense band at 748 cm^{-1} can be attributed to δ(Ar) vibrations. The bands at 770 and 732 cm^{-1} indicate that the adjacent positions in the aromatic ring are substituted [17, 20, 21]. In addition, a band found at 1537 cm^{-1} is assigned to C=N–N=C group [17–19]. In **2**–**6**, the clearly weakening and/or absence of the N–H and C=O stretching vibration bands at 1481 and 1691 cm^{-1} is consistent with deprotonation of the CONH groups and coordination to M(II). The C=N–N=C framework at l537 cm^{-1} in the ligand split into 1540–1554 and 1479–1525 cm^{-1} upon coordination to M(II). Bands at 501–560 cm^{-1} and 607–622 cm^{-1} are assigned to M–O (aromatic) and M(II)–N [22–27], respectively.

The UV-Vis spectra of the ligand and complexes were recorded using 10^{-4} mol L^{-1} solutions in methanol. All of the spectra are similar and associated with the conjugate system of fluorene. The spectra of the ligand and complexes have an intense and broad transition absorption band near 270 nm, with the shift from 274 nm to 267–271 nm via coordination. This absorption can be attributed to the intraligand charge transfer transition $\pi \rightarrow \pi^*$. Bands near 307 nm are also attributed to $\pi \rightarrow \pi^*$ charge transfer of fluorene, confirmed by no shift. The other peaks of the spectra in the visible region are very weak but give different, beautiful colors. For Co- and Cu-complexes, the absorptions at 680 and 659 nm are d-d transitions of the octahedral metal ions. The absorption maximum of $[Ni(ahfhz)_2] \cdot 2CH_3OH$ is at 650 and 720 nm due to $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition of six-coordinate Ni^{2+} ions.

Electrospray ionization mass spectroscopy, a soft ionization technique, has proved useful in providing the solution molecular weights of the formally neutral complexes. The methanol solution of the cobalt complex gave peaks at *m*/*z* 622 and 312 in ESI-MS. These peaks correspond to the cobalt core ion, $[Co(ahfhz)_2{+}H]^+$ and $[Co(ahfhz)_2 + 2H]^{2+}$, respectively.

The ^{1}H NMR of the ligand has a singlet at δ 1.84 ppm for the methyl protons, an overlap multiplet in the range δ 7.31–7.77 ppm for the fluorenyl protons 1-, 2-, 3-, 4-, 5-, 6- and 7-FluoH, and singlets at δ 9.87 and 10.00 ppm for the hydrazine protons [28]. In the ^{13}C NMR spectra of the ligand there are four peaks between 120 ppm and 130 ppm, concluded to be the eight isolated carbons of fluorenyl ring; the other two pair



Scheme 1. Synthesis of the complexes.

carbons are assigned to peaks at 140–150 ppm, but these peaks almost overlap. Two carbonyl carbons are at 165–175 ppm and the CH_3 carbon is at 20–30 ppm. The remaining peak at 80–85 ppm is attributed to the fluorenyl 9-carbon.

3.3. *Crystal structure of* $[Co(ahfhz)_2] \cdot 2CH_3OH$

Complex **3** crystallizes in the monoclinic system and space group $P2_1/n$. The crystal structure of **3** is presented in figure 2. Important bond distances and angles are presented in table 2.

In the crystal structure, the deprotonated ligand ahfhz$^-$ is a monoanionic tridentate ligand, one hydroxyl oxygen, one carbonyl oxygen and one hydrazide nitrogen in the ligand are bound to Co^{2+}. The coordination geometry of $[Co(ahfhz)_2] \cdot 2CH_3OH$ is best described as octahedral, with the equatorial plane defined by one hydroxyl oxygen atom O1 and one hydrazide nitrogen atom N1 and one carboxyl oxygen atom O3 from the one ahfhz$^-$ ligand, and one hydrazide nitrogen atom N3 from the other ahfhz$^-$ ligand; the two axial positions are occupied by one hydroxyl oxygen atom O4 and one carboxyl oxygen atom O6 (figure 3). The non-hydrogen atoms O1N1O3N3 of the ahfhz$^-$ ligand and Co(II) lie in a plane with an r.m.s deviation of 0.0294 Å. Both fluorenyl groups of ligand, C1–C13 and C17–C29, are nearly planar, with r.m.s deviations of 0.0459 Å and 0.0732 Å, respectively, and the dihedral angle between the two fluorenyl groups is 40.57(6)°. The Co(II) is nearly at the center of the square plane defined by two oxygen atoms and two nitrogen atoms from the two ahfhz$^-$ ligands, which are in an asymmetric

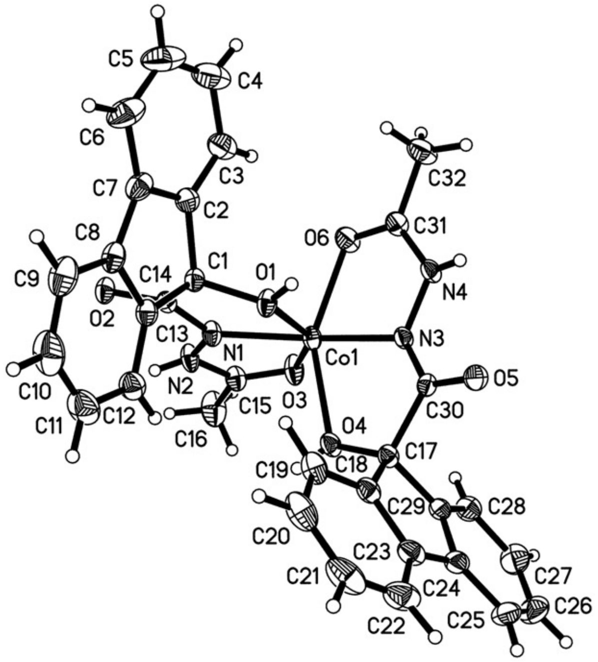


Figure 2. Perspective view of **3**; solvent molecules have been omitted for clarity.

configuration with a significant distortion, with bond lengths from 1.9769(17) Å to 2.2900(15) Å and bond angles from 70.86(6)° to 125.19(6)°, from the equatorial plane (table 2). Significant distortion also occurs at the axial positions between Co(II) and the donor atoms of the ahfhz⁻ ligands, with bond lengths 2.2078(16) Å and 2.1279(16) Å and bond angles ranging from 73.73(6)° to 106.10(7)° (table 2).

Table 2. Selected bond lengths (Å) and angles (°) in **3**.

Co1–O1	2.2900(15)	C1–C14	1.545(3)
Co1–N1	1.9879(17)	C14–O2	1.255(2)
Co1–O3	2.1140(15)	C14–N1	1.308(3)
Co1–O4	2.2078(16)	C17–O4	1.437(2)
Co1–N3	1.9769(17)	C17–C30	1.546(3)
Co1–O6	2.1279(16)	C30–O5	1.244(2)
N1–N2	1.392(3)	C30–N3	1.315(2)
N3–N4	1.397(2)	C15–N2	1.328(3)
C1–O1	1.430(2)	C31–N4	1.326(3)
N3–Co1–N1	156.79(7)	C30–N3–Co1	124.86(14)
N3–Co1–O3	125.19(6)	C1–O1–Co1	116.41(12)
N1–Co1–O3	77.37(6)	C15–O3–Co1	112.22(13)
N3–Co1–O6	77.71(6)	N4–N3–Co1	112.34(12)
N1–Co1–O6	106.10(7)	N2–N1–Co1	113.44(13)
O3–Co1–O6	99.30(6)	C17–O4–Co1	115.54(12)
N3–Co1–O4	73.73(6)	C30–N3–N4	116.67(17)
N1–Co1–O4	103.10(7)	C14–N1–N2	116.97(18)
O3–Co1–O4	91.15(6)	N1–C14–C1	113.23(18)
O6–Co1–O4	150.47(6)	N3–C30–C17	112.31(18)
N3–Co1–O1	86.28(6)	C15–N2–N1	115.65(19)
N1–Co1–O1	70.86(6)	C31–N4–N3	115.65(18)
O3–Co1–O1	148.17(6)	O5–C30–C17	120.75(18)
O6–Co1–O1	91.56(6)	O2–C14–C1	119.02(18)
O4–Co1–O1	93.91(6)	O1–C1–C14	107.31(16)
C14–N1–Co1	128.83(15)	O4–C17–C30	108.58(16)

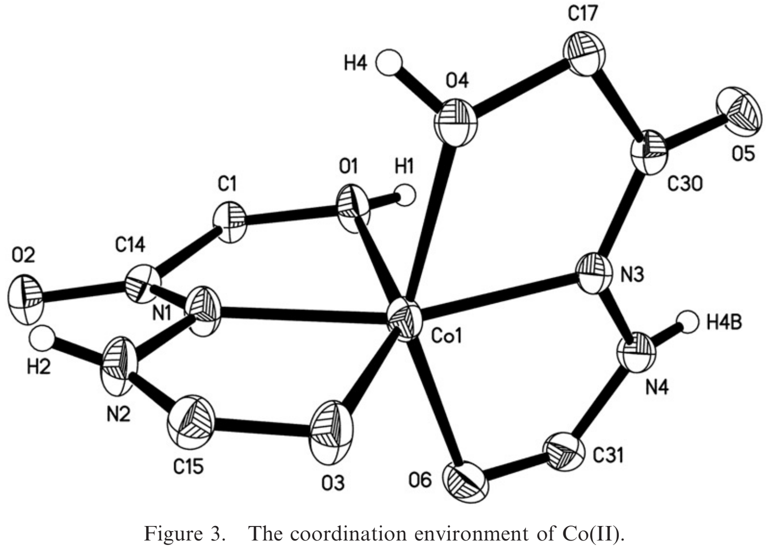


Figure 3. The coordination environment of Co(II).

There is a non-ionized O–H group in each of the ligands for $[\mathrm{Co(ahfhz)_2}]\cdot 2\mathrm{CH_3OH}$, although there is no hydrogen atom in the ionized hydroxyl group of the α-hydroxylated acid in the known binuclear copper carboxylate complexes [29–31], but it is very similar to that of $[\mathrm{Cu(C_{14}H_9O_3)_2(C_5H_5N)_2}]\cdot 2\mathrm{CH_3OH}$ [17]. The *N*-acetyl-9-hydroxyl-fluorene-9-hydrazide in **3** is a univalent ligand. In **3** the Co–O (non-ionized O–H group) bond lengths, 2.2900(15) Å and 2.2078(16) Å, are significantly longer than the Co–O (carboxyl) bond length (2.09 Å).

As listed in table 3, there are many kinds of intermolecular hydrogen bonds in **3**. Hydrogen bonds are between the hydrazide N–H group from coordinated $\mathrm{ahfhz^-}$ and the oxygen atom of carbonyl from the other $\mathrm{ahfhz^-}$ and the oxygen atom of the solvent methanol, the hydroxyl O–H group from coordinated $\mathrm{ahfhz^-}$ and the oxygen atom of the solvent methanol, and the hydroxyl O–H group from the solvent methanol and the oxygen atom of carbonyl from the $\mathrm{ahfhz^-}$. The $\mathrm{N{-}H \cdots O}$ and $\mathrm{O{-}H \cdots O}$ hydrogen bond distance ranges from 2.655(2) Å to 3.223(3) Å. These hydrogen bonds strengthen the crystal packing between $[\mathrm{Co(ahfhz)_2}]\cdot 2\mathrm{CH_3OH}$ molecules and form an infinite chain along the *c* axis. This aggregate can be regarded as the basic building block within the supramolecular structure. Furthermore $\mathrm{C{-}H} \cdots \pi$ hydrogen bonding interaction between the C–H of the fluorenyl groups, i.e. C4–H4A and C25–H25, and fluorenyl moieties of the ligands, i.e. the ring C17–C18–C23–C24–C29$^{\mathrm{i}}$ and the ring C2–C3–C4–C5–C6–C7$^{\mathrm{j}}$ (symmetry codes: (i) $1/2+x$, $1/2-y$, $-1/2+z$; (j) $-1+x$, y, z), lead to the supramolecular structure with $\mathrm{H} \cdots \mathrm{Cg}$ distance 3.37(3) Å and 3.13(3) Å, respectively.

3.4. *Antimicrobial activity*

Minimum inhibitory concentrations of **1**–**6** against *S. aureus*, *E. coli*, *B. subtilis* and *P. vulgaris* are listed in table 4. Except for *B. subtilis*, **1** does not have strong antimicrobial activities against the tested microorganisms. Similarly, except for $[\mathrm{Co(ahfhz)_2}]\cdot 2\mathrm{CH_3OH}$ (**3**) against *B. subtilis* and $[\mathrm{Cu(ahfhz)_2}]\cdot \mathrm{CH_3OH}$ (**5**) against *P. vulgaris*, the activities are less than expected. Moreover, in this study the complexes against Gram$^+$ bacteria *S. aureus* and *B. subtilis* are not better than against Gram$^-$ bacteria *E. coli* and *P. vulgaris* in antimicrobial activity [32]. While **1**–**6** had relatively weak antimicrobial effects against most of the tested microorganisms, with the most antibacterial activity of **1** and **3** was against *B. subtilis*, and **5** against *P. vulgaris*.

The results indicate that there is no synergistic effect for **1**. Conversely, we can see some antagonistic effect for Gram$^+$ bacteria *S. aureus* and *B. Subtilis*. Although the

Table 3. Hydrogen bond geometry (Å, °) in **3**.

$\mathrm{D{-}H \cdots A}$	D–H	$\mathrm{H \cdots A}$	$\mathrm{D \cdots A}$	$\mathrm{D{-}H \cdots A}$
$\mathrm{N4{-}H4B \cdots O2^a}$	0.86(2)	2.11(2)	2.891(2)	130(7)
$\mathrm{O8{-}H8 \cdots O2^a}$	0.73(3)	2.02(3)	2.754(3)	175(3)
$\mathrm{O7{-}H7 \cdots O5^b}$	0.83(3)	1.90(3)	2.729(3)	171(3)
$\mathrm{O4{-}H4 \cdots O7^c}$	0.83(3)	1.85(3)	2.655(2)	164(2)
$\mathrm{N2{-}H2 \cdots O8^d}$	0.75(2)	2.67(3)	3.223(3)	132(2)
$\mathrm{N2{-}H2 \cdots O5^d}$	0.75(2)	2.33(2)	2.908(3)	134(2)
$\mathrm{O1{-}H1 \cdots O8}$	0.84(3)	1.83(3)	2.672(3)	176(3)

Symmetry codes: $^{a}x-1/2, -y+1/2, z-1/2$; $^{b}x+1/2, -y+1/2, z-1/2$; $^{c}x, y, z+1$; $^{d}x+1/2, -y+1/2, z+1/2$.

Table 4. Minimum inhibitory concentration (MIC) of **1**–**6** in $\mu g\,mL^{-1}$.

	Compounds					
Microorganisms	**1**	**2**	**3**	**4**	**5**	**6**
E. coli (Gram$^-$)	1600	1600	800	1600	800	1600
B. subtilis (Gram$^+$)	25	100	25	1600	200	800
P. vulgaris (Gram$^-$)	800	1600	400	1600	25	1600
S. aureus (Gram$^+$)	400	1600	200	1600	1600	1600

data available are limited and it is risky to correlate the structural features to the bioactivity of these compounds, the decrease in the efficiency of **2**–**6** may be assigned to the zero charge of the central core. The charge can increase the affect on bacteria.

4. Conclusion

The five metal complexes were the first example of complexes containing M(II) as central ion with *N*-acetyl-9-hydroxyl-fluorene-9-hydrazide. In the article, we described the synthesis and structural characterization of Hahfhz and five metal complexes. The complex $[Co(ahfhz)_2]\cdot 2CH_3OH$ contains two ahfhz$^-$ and two solvent methanols, with a distorted octahedral geometry. The crystal structure packing, mediated by N–H⋯O, O–H⋯O and C–H⋯π hydrogen bonding interactions, leads to the generation of aggregates of supramolecular structure. Hydrogen bond distances of N–H⋯O and O–H⋯O range from 2.655(2) Å to 3.223(3) Å. Antibacterial screening data (MIC) showed that the cobalt and copper complexes and **1** have moderate antimicrobial activity. The results indicate that five metal complexes do not have synergistic effect with **1**. Conversely, we can see some antagonistic effect for Gram$^+$ bacteria *S. aureus* and *B. subtilis*. The decrease in the efficiency of complexes **2**–**6** may be assigned to the lack of charge of the central core.

Supplementary material

CCDC 619650 contains the supplementary crystallographic data for **3**. The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44 1223 336 033; Email: deposit@ccdc.cam.ac.uk).

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References

[1] G. Schneider. *Ann. Rev. Plant. Physiol.*, **21**, 499 (1970).
[2] G. Schneider, D. Erdmann, S. Lust, G. Mohr. *Nature*, **208**, 1013 (1965).

[3] L.F. Fieser, K.L. Williamson. *Organic Experiments*, 7th Edn, D.C. Heath and Company, Lexington, Massachusetts, US (1992).
[4] Y.L. Feng, S.X. Liu. *Chin. J. Struct. Chem.*, **21**, 142 (2002).
[5] Z.P. Deng, S. Gao, L.H. Huo, H.J. Zhao. *Chin. J. Inorg. Chem.*, **22**, 567 (2006).
[6] S. Gao, L.H. Huo, H. Zhao, C.S. Gu, J.G. Zhao. *Chin. J. Inorg. Chem.*, **21**, 862 (2005).
[7] C. Vadapalli, T. Pakkirisamy, F.B. James, S. Alexander. *J. Am. Chem. Soc.*, **127**, 11556 (2005).
[8] P.J. Rohith, K. Lee, B.J. Kim, B.J. Suh, H. Rhee, M.S. Lah. *Inorg. Chem.*, **44**, 7109 (2005).
[9] S.X. Liu, S. Lin, B.Z. Lin, C.C. Lin, J.Q. Huang. *Angew. Chem. Int. Ed.*, **40**, 1084 (2001).
[10] J. Dou, M. Liu, D. Li, D. Wang. *Eur. J. Inorg. Chem.*, **23**, 4866 (2006).
[11] M.X. Yang, S. Lin, L.J. Chen, S.X. Liu. *Chin. J. Inorg. Chem.*, **19**, 433 (2003).
[12] L.F. Jin, F.P. Xiao, G.Z. Cheng, Z.P. Ji. *Inorg. Chem. Commun.*, **9**, 758 (2006).
[13] L.F. Jin, F.P. Xiao, G.Z. Cheng, Z.P. Ji. *J. Organomet. Chem.*, **691**, 2909 (2006).
[14] Bruker AXS Inc., *SMART APEX* (*Version 5.628*), *SAINT*+(*Version 6.45*) *and SHELXTL-NT* (*Version 6.12*), Bruker AXS Inc., Madison, Wisconsin, US (2001).
[15] G.M. Sheldrick. *SHELXS*97 *and SHELXL*97, University of Göttingen, Germany (1997).
[16] S.N. Rao, K.N. Munshi, N.N. Rao, M.M. Bhadbhade, E. Suresh. *Polyhedron*, **18**, 2491 (1999).
[17] Z. Yu, D.M. Xu, S.X. Liu. *Inorg. Chim. Acta*, **294**, 163 (1999).
[18] H. Adams, D.E. Fenton, G. Minardi, E. Mura, A.M. Pistuddi, C. Solinas. *Inorg. Chem. Commun.*, **3**, 24 (2000).
[19] D.K. Rastogi, S.K. Sahni, V.B. Rana, K. Dua, S.K. Dua. *J. Inorg. Nucl. Chem.*, **41**, 21 (1979).
[20] L.J. Bellary. *The Infrared Spectra of Complex Molecules*, 2nd Edn, Vol. II, Chapman and Hall, London (1980).
[21] J.G. Wu. *Technology and Application of the Modern Fourier Transform Infrared Spectra*, Science and Technology Reference Publication Press, Beijing (1994).
[22] G. Blyholder, N. Ford. *J. Phys. Chem.*, **68**, 1496 (1964).
[23] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Edn, Wiley, New York, US (1986).
[24] J.M. Rigg, E. Sherwin. *J. Inorg. Nucl. Chem.*, **27**, 653 (1965).
[25] E.B. Kipp, R.A. Haines. *Can. J. Chem.*, **47**, 1073 (1969).
[26] J.R. Ferraro, W.R. Walkers. *Inorg. Chem.*, **4**, 1382 (1965).
[27] C.W.R. Canham, A.B.P. Lever. *Spectrosc. Lett.*, **6**, 109 (1973).
[28] Y.P. Yu, D.L. Zhu. *Chem. J. Chinese Universities*, **13**, 1590 (1992).
[29] S.X. Liu. *Acta Crystallogr., Sect. C*, **48**, 22 (1992).
[30] S.X. Liu, Y.P. Yu. *Acta Crystallogr., Sect. C*, **48**, 652 (1992).
[31] Y.P. Yu, D.L. Zhu, S.X. Liu. *Acta Crystallogr., Sect. C*, **52**, 628 (1996).
[32] A.R. McCutheon, S.M. Ellis, R.E.W. Hancock, G.H.N. Towers. *J. Ethnopharmacol.*, **37**, 213 (1992).