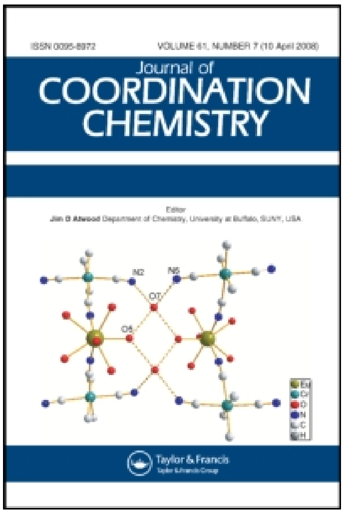

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Synthesis and characterization of three ionic pairs of Fe(II) and Co(II) complexes with tridentate salicylideneglycine

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Synthesis and characterization of three ionic pairs of Fe(II) and Co(II) complexes with tridentate salicylideneglycine

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Three new transition metal complexes, $[Fe^{II}(H_2O)_6][(C_9H_7NO_3)_2Fe^{II}]\cdot H_2O$ (**1**), $H[K(H_2O)_3][(C_9H_7NO_3)_2Co^{II}]\cdot H_2O$ (**2**), and $[Co^{II}(H_2O)_6][(C_9H_7NO_3)_2Co^{II}]\cdot H_2O$ (**3**), with salicylideneglycine have been synthesized and characterized by elemental analysis, IR spectra, UV-Vis spectroscopy, and X-ray crystallography. The structure analyses indicate that the tridentate salicylideneglycine binds through aliphatic nitrogen, phenoxy, and carboxylic oxygen in the anion. There are many inter- and intra-molecular hydrogen bonds among lattice water, the anion, and the cation to form a 3-D network. The thermogravimetric analyses and the quantum chemistry calculations of compounds **1**, **2**, and **3** are also discussed.

Keywords: Complexes; Salicylideneglycine ligand; Crystal structure; Hydrogen bonds

1. Introduction

Various salen-type Schiff bases containing nitrogen and oxygen donors which play an important role in biological systems and represent interesting models for metalloenzymes are capable of forming complexes with metal ions which can exhibit unusual coordination, high thermodynamic stability, and kinetic inertness [1–4]. There have been numerous reports of transition metal complexes containing salen ligands [5–17], but few reports of the crystal structures of complexes with salicylideneglycine, whose structure is shown in figure 1. In an earlier paper, we reported crystal structures of neutral complexes with salicylideneglycine ($C_9H_7NO_3$): $(C_9H_7NO_3)Cu(C_3H_4N_2)$, $(C_9H_7NO_3)Zn(C_3H_4N_2)_2$, $(C_9H_7NO_3)_2Ni_2(C_3H_4N_2)_4$, and $(C_9H_7NO_3)Ni(C_3H_4N_2)_2(C_4H_5N_2O)\cdot CH_3OH\cdot 0.5H_2O$ [18]. Transition metal complexes with Schiff bases mimic biological sites [19–25], so we tested SOD-like activities for some complexes with salicylideneglycine ligands and obtained significant results. In this article, we report three new supramolecular complexes with salicylideneglycine: $[Fe^{II}(H_2O)_6]$

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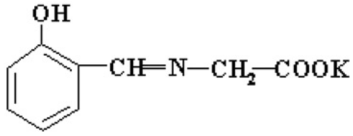

Figure 1. The structure of potassium salt of salicylideneglycine.

$[(C_9H_7NO_3)_2Fe^{II}] \cdot H_2O$ (**1**), $H[K(H_2O)_3][(C_9H_7NO_3)_2Co^{II}] \cdot H_2O$ (**2**), and $[Co^{II}(H_2O)_6][(C_9H_7NO_3)_2Co^{II}] \cdot H_2O$ (**3**), which have been structurally characterized.

2. Experimental

2.1. *Physical measurements*

Elemental analyses were performed on a P. E 240C automatic analyzer. IR spectra were determined on a JASCO FT/IR-480 PLUS Fourier Transform spectrometer (200–4000 cm^{-1}, with pressed KBr pellets); UV-Vis spectra were obtained on a JASCO V-570 UV-Vis spectrometer (200–1100 nm, in methanol solution for **1** and as solids for **2** and **3**).

2.2. *X-ray crystallography*

Crystals of **1**, **2**, and **3** were mounted on a glass fiber for X-ray measurement. Reflection data were collected at room temperature on a Bruker AXS Smart APEX II CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and ψ scan mode. All the measured independent reflections were used in the structural analyses, and semi-empirical absorption corrections were applied using SADABS. Crystal data, data collection, and refinement details are summarized in table 1; the quality of the crystal of **1** is poor and the structural refinement gives higher *R*-value of 0.0961.

The structures were solved by direct methods using SHELXS-86 and refined using SHELXTL-97. All non-hydrogen atoms were refined anisotropically and contributions of hydrogens were included in calculated positions, constrained to ride on their carbons with group U_{iso} values assigned. Atomic scattering factors and anomalous dispersion terms were as in SHELXTL-97. The drawings were made with diamond.

2.3. *Thermogravimetric assay of 1, 2, and 3*

Thermogravimetric analyses (TGA) were carried out on a Perkin Elmer Diamond TG/DTA instrument. The samples are initially heated for 1 h at 50°C to remove air. During the simple ramping experiment, weight changes were recorded as a function of temperature for a 10°C min^{-1} temperature ramp between 50 and 1000°C for **1**, **2**, and **3** under nitrogen. The masses of **1**, **2**, and **3** are 3.515, 2.804, and 2.922 mg, respectively.

Table 1. Crystallographic data for **1**, **2** and **3**.

Formula	$C_{18}H_{19}N_2O_{10}Fe_{1.25}$	$C_{18}H_{23}N_2O_{10}CoK$	$C_{18}H_{23}N_2O_{10}Co_{1.50}$
M ($g\,mol^{-1}$)	493.16	525.41	515.78
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$C2/c$	$P2_1/c$	$Pbcn$
Unit cell dimensions (Å, °)			
a	38.622(8)	19.017(4)	9.560(4)
b	12.148(2)	9.6823(19)	12.253(5)
c	9.3474(19)	11.848(2)	36.854(15)
α	90.00	90.00	90.00
β	102.88(3)	92.06(3)	90.00
γ	90.00	90.00	90.00
V (Å^3)	4275.2(15)	2180.1(8)	4317(3)
Z	8	4	8
D_{Calcd}	1.532	1.601	1.587
Crystal size (mm^3)	0.21 × 0.15 × 0.1	0.03 × 0.10 × 0.1	0.02 × 0.06 × 0.1
$F(000)$	2028	1084	2124
μ(Mo-Kα) (cm^{-1})	0.925	1.036	1.223
θ (°)	1.76 to 25.00	3.00 to 25.00	2.21 to 25.00
Reflections collected	10552	3838	20395
Independent reflections [$I > 2\sigma(I)$]	3767	3236	3812
Parameters	294	309	318
$\Delta(\rho)$ (e Å^{-3})	0.419 and −0.573	0.421 and −0.561	0.604 and −0.633
Goodness-of-fit	1.079	1.075	1.032
R[a]	0.0451 (0.0649)[b]	0.0407 (0.0494)[b]	0.0473 (0.0763)[b]
wR_2[a]	0.1162 (0.1262)[b]	0.1092 (0.1133)[b]	0.1116 (0.1239)[b]

[a] $R = \|F_o|-|F_c\|/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2/[\Sigma(w(F_o^2)^2]^{1/2}$; $[F_o > 4\sigma(F_o)]$.
[b] Based on all data.

2.4. *Methods of quantum chemistry calculation*

MP2 calculations at 3-21G*(6d, 7f) basis set levels were carried out for complexes with Gaussian 03W program. The calculation included 41, 47, and 48 atoms; 289, 518, and 544 basis functions; 489, 1104, and 1160 primitive Gaussians for **1**, **2**, and **3**, respectively. The parameters of the molecular structures come from the crystal structure data, and the molecular point groups and their symmetry (C_s) are also considered. The electronic structures and bonding character of the complexes were analyzed with *ab initio* calculations and Natural Bonding Orbital analysis. The result of calculation gives the constitution and the energy of the molecular orbital and NBO atomic charge.

2.5. *Preparations*

All the starting materials were of analytical grade. The Schiff base (KHL: salicylideneglycine) was prepared by modified literature method [26] and all other reactants were used as purchased. All reactions were carried out at room temperature.

2.5.1. Preparation of $[Fe^{II}(H_2O)_6][(C_9H_7NO_3)_2Fe^{II}]\cdot H_2O$ (1). A solution of KHL (0.11 g, 0.5 mmol) in methanol (10 mL) was added to a methanol solution (15 mL) containing $FeSO_4\cdot 2H_2O$ (0.08 g, 0.5 mmol). The dark red-brown mixture was stirred for 3 h and then concentrated to 5 mL volume. The solution was put into a column with silica gel to further separate using mixed hexane and acetone. After the resulting solution was stored for about 30 days, several black-red crystals were obtained, washed with methanol and ethanol extensively, and dried under vacuum to afford 0.30 g of the product in 60.0% yield (based on $FeSO_4 \cdot H_2O$). Anal. Calcd for $C_{18}H_{19}N_2O_{10}Fe_{1.25}$: C, 43.80; H, 3.85; N, 5.68. Found: C, 43.96; H, 3.62; N, 5.79%. IR (KBr, ν cm^{-1}): 3354m, 2921m, 1634s, 1599s, 1541m, 1467s, 1443m, 1371s, 1331m, 1198m, 1149s, 1068s, 763s, 540m, 454w, 373w.

2.5.2. Preparation of $H[K(H_2O)_3][(C_9H_7NO_3)_2Co^{II}] \cdot H_2O$ (2) and $[Co^{II}(H_2O)_6][(C_9H_7NO_3)_2Co^{II}] \cdot H_2O$ (3). An ethanol solution of KHL 0.5 mmol (0.11 g) and Co $(CH_3COO)_2 \cdot H_2O$ (0.25 mmol, 0.06 g) was stirred for 3 h. The dark yellow-brown solution was stored for 35 days and dark brown crystals suitable for X-ray were obtained and dried under vacuum to afford 0.10 g of the product, 74.3% yield (based on $Co(CH_3COO)_2 \cdot H_2O$). Anal. Calcd for $C_{18}H_{23}N_2O_{10}CoK$: C, 41.11; H, 4.38; N, 5.33. Found: C, 40.96; H, 4.25; N, 5.23%. IR (KBr, ν cm^{-1}): 3440m, 3053m, 2925m, 1654s, 1600s, 1537m, 1466s, 1449m, 1391s, 1355m, 1303m, 1201m, 1150s, 1082s, 755s, 643s, 539m, 475w, 432w, 329w.

The preparation of **3** is the same as that of **2**, but having 1 : 1 molar ratio of $Co(CH_3COO)_2 \cdot 2H_2O$ and KHL. About 0.33 g of the product was obtained in 63.5% yield (based on $Co(CH_3COO)_2 \cdot 2H_2O$). Anal. Calcd for $C_{18}H_{23}N_2O_{10}Co_{1.50}$: C, 41.88; H, 4.46; N, 5.43%. Found: C, 41.66; H, 4.53; N, 5.31%. IR (KBr, νcm^{-1}): 3396m, 2926m, 1652s, 1600s, 1537m, 1449s, 1392s, 1370m, 1199m, 1149m, 1131s, 1081s, 754s, 669s, 538m, 475w, 438w, 370w.

3. Results and discussion

3.1. *Spectra*

3.1.1. IR spectra. The infrared spectra of **1**, **2**, and **3** are consistent with the structural data. Strong bands for **1**, **2**, and **3** are at 1634 cm^{-1}, 1654 cm^{-1}, and 1652 cm^{-1}, respectively, are attributed to the stretching of C=N from the Schiff base [26]. Bands at 1599 cm^{-1}, 1371 cm^{-1} for **1**; 1600 cm^{-1}, 1355 cm^{-1} for **2** and 1600 cm^{-1}, 1370 cm^{-1} for **3**, respectively, are assigned to asymmetric and symmetric stretching vibrations of the carboxylate from the Schiff base. The spectra have bands for **1**, **2**, and **3** in the range 1537–1541 cm^{-1} and 754–763 cm^{-1}, assigned to C=C of aromatic and C–H aromatic stretching vibration, respectively. For **1**, **2**, and **3** bands at 1149 cm^{-1}, 1150 cm^{-1}, and 1149 cm^{-1}, respectively, are due to C–N stretch. Three bands for ν_{M-N} at 538–540 cm^{-1}, $\nu_{M-O\ \mathrm{hydroxyl}}$ at 432–458 cm^{-1} and $\nu_{M-O\ \mathrm{carboxyl}}$ at 370–373 cm^{-1} substantiate the Schiff base coordination to the metals [26].

3.1.2. UV-Visible absorption spectra. The electronic absorption spectrum of **1** is recorded in CH_3OH and that of **2** and **3** as solids. Electronic absorption spectra of **2** and **3** are similar. The sharp and strong high-energy absorption bands at 208, 226, and 266 nm for **1**, 272 nm for **2** and **3** are assigned as transitions of the aromatic-like chromophore from the Schiff base (LLCT). A band at 508 nm for **1** can be assigned to the d → d* transition of $Fe^{II}[^5T_{2g} \rightarrow {}^5E_g]$, while bands at 698 and 546 nm for **2**, and 702 and 570 nm for **3** are attributed to $Co^{II}[^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)]$ and $Co^{II}[^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)]$, respectively.

3.2. *Crystal structures*

Representations of $[Fe^{II}(H_2O)_6][(C_9H_7NO_3)_2Fe^{II}]\cdot H_2O$ (**1**), $H[K(H_2O)_3][(C_9H_7NO_3)_2Co^{II}]\cdot H_2O$ (**2**), and $[Co^{II}(H_2O)_6][(C_9H_7NO_3)_2Co^{II}]\cdot H_2O$ (**3**) with the atom-numbering schemes are given in figures 2–4, respectively. The principal bond lengths and angles are listed in "Supplementary material". All the complexes consist of mononuclear coordination anion and a coordination cation, and the anions have very similar coordinate modes.

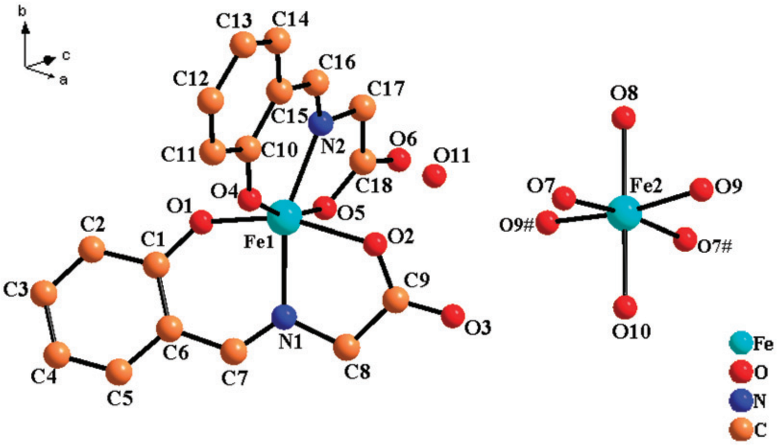

Figure 2. The structure of **1**. Symmetry transformations used to generate equivalent atoms: #: $-x+1$, y, $-z+3/2$.

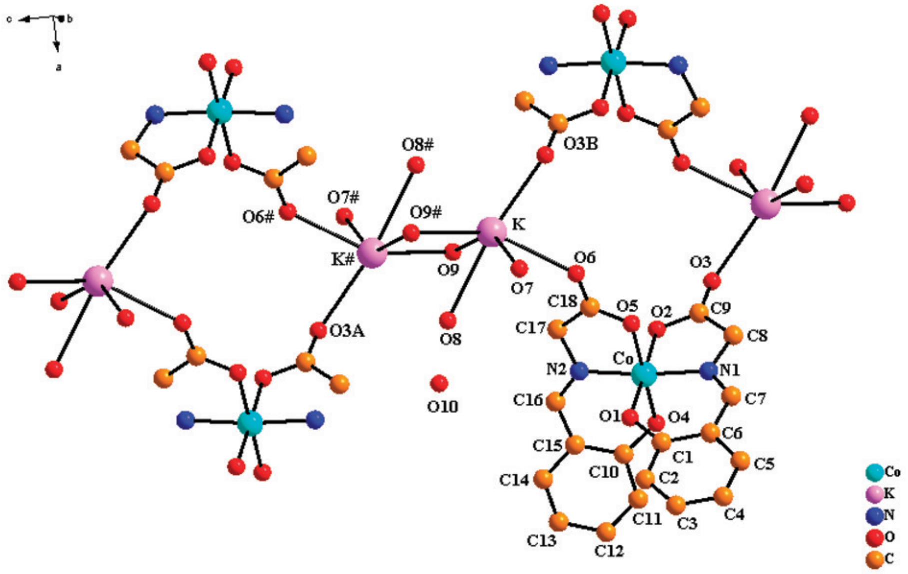

Figure 3. The structure of **2**. Symmetry transformations used to generate equivalent atoms: #: $1-x$, $1-y$, $2-z$; A: x, y, $1+z$; B: $1-x$, $1-y$, $1-z$. A: x, y, $1+z$. B: $1-x$, $1-y$, $1-z$.

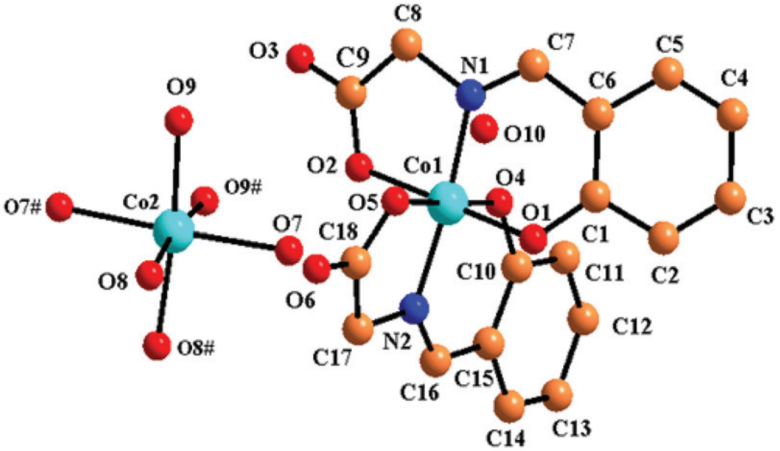

Figure 4. The structure of **3**. Symmetry transformations used to generate equivalent atoms: #: $-x+1$, y, $-z+1/2$.

For the anions: the metals of **1**, **2**, and **3** are six coordinate with a slightly distorted octahedron. The six coordination sites are occupied by four O atoms and two N atoms, from two Schiff-base ligands (salicylideneglycine). The distortion of three octahedral structures is different. For **1**, the iron lies 0.0122(8) Å above the least-squares plane defined by the four donors (O1, O2, O4, and O5) and the average deviation of the atoms from the coordination plane is −0.0122(10) Å. The axial positions are occupied by N1 and N2 and form a N1–Fe1–N2 angle of 159.18(9)°. The structures of **2** and **3** are nearly the same, and similar to the anion of **1**. For **2**, the cobalt atom lies in the O1–O4–O2–O5 coordination plane and N1 and N2 occupy the axial positions, forming a N1–Co–N2 angle of 174.1(1)°. The average deviation of the four atoms from the coordination plane is −0.00005(11) Å. For **3**, the cobalt lies in the O1–O4–O2–O5 coordination plane and the N1 and N2 occupy the axial positions, forming a N1–Co1–N2 angle of 173.5(1)°. The average deviation from the coordination plane is 0.00005(13) Å. Comparing the N–M–N angles in **1**, **2**, and **3**, compound **1** is more distorted than the compounds **2** and **3**. The orders of the average distances of M–N and M–O and the average angles of N–M–O are as follows: **1** (2.086(2) Å) > **2** (1.887(2) Å) ≈ **3** (1.889(6) Å); **1** (1.991(2) Å) > **2** (1.892(2) Å) ≈ **3** (1.897(5) Å); **1** (81.28(9)°) < **2** (90.31(10)°) ≈ **3** (90.55(2)°), respectively.

In the coordination cations for **1**, the Fe2 is coordinated to six water molecules with distances of 2.038(0) Å (Fe2–O8), 2.065(0) Å (Fe2–O10), 2.082(1) Å (Fe2–O7 and Fe2–O7#: $1-x$, y, $1.5-z$), and 2.051(13) Å (Fe2–O9 and Fe2–O9#: $1-x$, y, $1.5-z$). For **2**, K^+ is six-coordinate with three kinds of coordinated oxygens: (i) K–O6 (O3#: $1-x$, $1-y$, $1-z$) which is from the uncoordinated carboxyl oxygen of the Schiff base; (ii) K–O7 (O8) which is from the lattice water; (iii) K–O9 (O9#: $1-x$, $1-y$, $2-z$), which is also from the lattice water and bridging another K# (#: $1-x$, $1-y$, $2-z$) forming a $[K(\mu_2\text{–}O)_2(H_2O)_2]$ unit, connecting four $[(C_9H_7NO_3)_2Co]^{2-}$ anions forming a tetramer leading to a chain along c direction within the distance range 2.693(3)–3.5479(2) Å. For **3**, the cation has cobalt six coordinate with water. The bond distances

Table 2. Hydrogen bonds of **1**, **2** and **3**[b].

D–H···A	D(D–H) (Å)	d(H···A) (Å)	D–H–A (°)	d(D···A) (Å)
Proposed hydrogen bonds for complex **1**				
O7–H7A···O5a	0.819	1.943	173.71	2.758
O9–H9A···O3b	0.820	2.008	157.93	2.785
O10–H10A···O3c	0.821	2.032	149.15	2.769
O11–H11B···O2	0.946	1.866	169.00	2.793
Proposed hydrogen bonds for complex **2**				
O9–H9C···O3d	0.678	2.289	155.63	2.920
O9–H9B···O6e	1.012	1.928	145.74	2.822
O8–H8A···O5f	0.941	2.043	160.31	2.946
O7–H7A···O6g	0.820	2.256	158.10	3.033
Proposed hydrogen bonds for complex **3**				
O9–H9A···O9h	1.151	2.248	130.51	3.120
O10–H10B···O5i	0.956	1.933	173.66	2.885
O7–H7B···O10	0.836	1.887	166.73	2.707
O7–H7A···O2j	0.849	2.042	169.62	2.882
O8–H7A···O9	0.990	2.196	122.85	2.857
O8–H8A···O3k	0.869	1.882	155.68	2.698

[b] Symmetry transformation used to generate equivalent atoms: a: $x, y, 1+z$. b: $1-x, y, 3/2-z$. c: $x, -y, 1/2+z$. d: $x, -y+5/2, z+1/2$. e: $-x+1, y+1/2, -z+1/2$. f: $x, -y+3/2, z+1/2$. g: $-x+1, y-1/2, -z+1/2$. h: $-x+1, y, -z+1/2$. *i*: $x-1/2, y+1/2, -z+1/2$. j: $x+1/2, y+1/2, -z+1/2$. *k*: $-x+1, y+1, -z+1/2$.

of the Co2–O (Co2–O7/O7#, Co2–O8/O8#, and Co2–O9/9#, #: $-x+1, y, -z+1/2$) are in the range 2.050(3)–2.122(4) Å.

For compounds **1**, **2**, and **3**, in addition to the electrostatic interaction, many hydrogen bonds exist. There are four kinds of hydrogen bonds among the lattice water, Schiff base, and $[Fe(H_2O)_6]^{2+}$ for **1**; four kinds of hydrogen bonds among the lattice water, Schiff base, and $[HK(H_2O)_3]^{2+}$ for **2**; and six kinds of hydrogen bonds among $[Co(H_2O)_6]^{2+}$, lattice water, and the Schiff base of **3** with the distances ranging from 2.22 to 3.345 Å and 2.698 to 3.120 Å. In addition, there are also weak interactions among the lattice water, the cation and the anion for **1**, **2**, and **3**. Details of hydrogen bonds are listed in table 2.

3.3. *Thermogravimetric analyses*

The TG–DTG–DTA curves of **1** show three stages of thermal decomposition. The first from 101 to 311°C with mass loss of 1.85% corresponds to loss of one lattice water (calculated value 1.82%). The second stage from 311 to 377°C with mass loss of 1.72% is due to loss of one water molecule, agreeing well with the TG curve (1.82%). The third stage from 377 to 746°C, with mass loss of 3.52%, corresponds to loss of two water molecules (calculated value 3.64%). The DTA curve of **1** indicates an exothermic–endothermic process.

For **2**, the TG–DTG–DTA curves indicate five steps: the first from 79 to 168°C with loss of 3.95% is due to loss of one lattice water (calculated value 3.43%). The second from 168 to 235°C with 4.20% weight loss is due to the loss of a water molecule (calculated value 3.43%). The third step from 235 to 366°C with 16.01% weight loss was due to loss of two water molecules and one CO_2 from Schiff base (calculated value

15.23%). The fourth and fifth steps from 366 to 521°C and from 521 to 667°C with 7.83 and 9.23% weight loss correspond to loss of a CO_2 and a NO_2 from the Schiff base (calculated 7.42 and 8.37%).

There are three stages of thermal decomposition for **3**. The first from 78 to 142°C as mass loss of 3.10% corresponds to loss of two lattice water molecules (calculated 3.50%) in an exothermic process. The second occurs from 142 to 361°C with mass loss of 7.25% due to loss of four coordinated water molecules around Co_2 (6.99%) in an endothermic process. The third stage from 361 to 823°C has mass loss of 8.69% due to loss of a CO_2 from the Schiff base (8.55%) in an exothermic process. Although coordination modes of the Schiff base to metals are the same, decomposition processes are different.

3.4. *Calculations*

Frontier orbits and nearby molecular orbits are the most important factors to the stability. The larger the difference between the frontier orbits, the more stable the structure. Frontier molecular orbital symmetry and eigenvalues in Hartree for **1**, **2**, and **3** (see Supplemental material): HOMO: −0.31464, −0.25616, and −0.27142; LUMO: −0.11676, −0.10610, and −0.19513. The energy values of ΔE ($\Delta E = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$) are 0.19788, 0.15006, and 0.07629, respectively, for **1**, **2**, and **3**, showing that the stability is **1** > **2** > **3**.

4. Conclusion

In this article we report three similar complexes with the same tridentate salicylideneglycine. For the anions, the coordination modes are all similar. The coordination behavior of the tridentate salicylideneglycine depends on the nature of the metal and also on the anion of the starting metal salt. We obtained cobalt(II) crystals using $Co(CH_3COO)_2 \cdot H_2O$ but not using $CoCl_2 \cdot H_2O$. The complexes with salicylideneglycine are expected to have several biological sites as models of some amino enzymes. This work is proceeding in our research group.

Supplementary material

Tables of atomic coordinates, an isotropic thermal parameter, and complete bond distances and angles have been deposited with the Cambridge Crystallographic Data Center. Copies of this information may be obtained free of charge by quoting the publication citation and deposition numbers CCDC: 653966 for **1**, 653968 for **2**, and 653967 for **3**, from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44–1223–336033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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