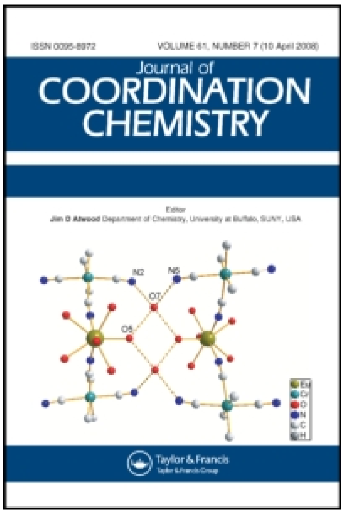

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, structures and properties of cobalt(III) and iron(III) complexes with a new triazamacrocycle, 1,4-diacetate-1,4,7-triazacyclodecane

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To cite this Article Guo, Hui , Shao, Xiao-Jun , Li, Jun , Wang, Chen , Yang, Gao-Mai , Duan, Min-Yue and Zhang, Feng-Xing(2008) 'Synthesis, structures and properties of cobalt(III) and iron(III) complexes with a new triazamacrocycle, 1,4-diacetate-1,4,7-triazacyclodecane', Journal of Coordination Chemistry, 61: 22, 3610 — 3619

To link to this Article: DOI: 10.1080/00958970802090148

URL: http://dx.doi.org/10.1080/00958970802090148

Journal of Coordination Chemistry
Vol. 61, No. 22, 20 November 2008, 3610–3619

Synthesis, structures and properties of cobalt(III) and iron(III) complexes with a new triazamacrocycle, 1,4-diacetate-1,4,7-triazacyclodecane

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(*Received 11 September 2007; in final form 29 October 2007*)

A new bidisplaced acetate functionalized pendant arm derivative, 1,4-diacetate-1,4,7-triazacyclodecane (**L**) and its corresponding Co(III), Fe(III) complexes [CoLCl] (**1**) and $[FeLCl]_2 \cdot 3H_2O$ (**2**) were synthesized and characterized by elemental analysis, IR spectra, UV–Vis spectra, HNMR, MS, XPRD, TGA and single-crystal X-ray diffraction analysis. The crystal structure shows the metal ions in the complexes have similar coordination six-coordinate, by three nitrogens and two oxygens of the chelate ligand, and a chloride. Through calculation of the twist angle, we discover 1 forms a distorted octahedral geometry while 2 forms a distorted-prismatic geometry. In 2, there are abundant hydrogen bonds between the oxygen atoms of water and the nitrogens and oxygens of the ligand, resulting in a two-dimensional supramolecular network with a regular triatomic water cluster. The thermal gravimetric analyses of the two complexes are also given.

Keywords: Macrocyclic triamine; 1,4-Diacetate-1,4,7-triazacyclodecane; Co(III) complex; Fe(III) complex; Crystal structure

1. Introduction

Metal complexes containing macrocyclic triamines and their derivatives have diverse applications as inorganic medicinal compounds, anion or molecule receptors, molecular sensors and mimics for hydrolytic metal-enzymes [1–6]. The nine-member 1,4,7-triazacyclononane (TACN) was one of the most studied and much effort has been devoted to hexadentate ligands with three identical pendants, for example, the derivatives of TACN with three pendant acetate [7–9], hydroxypropyl [10], pyridyl [11, 12] and phosphonate [13] groups. Functionalized ligands with only one or two pendant donors are less frequently reported because of their difficulty for synthesis [14,15]. For the ten-member 1,4,7-triazacyclodecane (TACD), its derivatives were reported only rarely [16, 17]. Metal complexes containing derivatives of TACD with only two pendant donors have not been reported.

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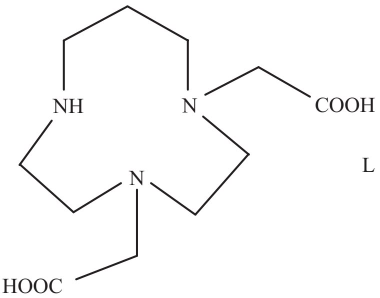
Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970802090148



Scheme 1. The ligand structure.

Some transition metal complexes with asymmetric 1,4,7-triazacyclodecane (TACD) ligands have been synthesized by us, and they gave various structural characteristics [18–20]. In order to further study complexes containing macrocyclic ligands, herein, we report a new TACD derivative ligand, 1,4-diacetate-1,4,7-triazacyclodecane (**L**) (Scheme 1) and its corresponding Co(III), Fe(III) complexes [CoLCl] (**1**) and $[FeLCl]_2 \cdot 3H_2O$ (**2**).

2. Experimental

2.1. *Materials*

The macrocyclic triamine 1,4,7-triazacyclodecane trihydrochloride (tacd · 3HCl) was prepared as described previously [21, 22]. Other reagents were of analytical grade from commercial sources and used without purification.

2.2. *Physical measurements*

Elemental analyses (C, H and N) were performed by a Vario EL-III instrument. Infrared spectra were recorded on an Equinox55 spectrophotometer in the range of 4000–400 cm^{-1} using a KBr pellet. UV–Vis spectra were recorded on a TU-1800 spectrophotometer in water. ^1H NMR spectra were recorded on a Varian INOVA-400MHz spectrometer with TMS as internal standard in D_2O at room temperature. FAB-MS mass spectra were obtained with a JEOL HX-110HF double focusing spectrometer operating in the positive ion detection mode. The XPRD patterns were with a Rigaku D/Max 3III diffractomer at a scanning rate of $4^\circ \min^{-1}$. TGA analysis were performed on a Netzsch STA 449C instrument in flowing N_2 with a heating rate of $10^\circ C \min^{-1}$.

2.3. *Synthesis*

2.3.1. Ligand (L). An aqueous solution (10 mL) of chloroacetic acid (0.65 g, 7.7 mmol) and $LiOH \cdot 0.5H_2O$ (1.4 g, 58 mmol) were added to an aqueous solution (10 mL) of tacd · 3HCl (0.954 g, 3.85mmol). The resulting mixture was stirred for 48 h at 45°C, and the pH was maintained around 10 ± 0.5 by adding small portions of solid $LiOH \cdot 0.5H_2O$ during the reaction. The pH of the solution was adjusted to 2.0 with 6 M HCl after the reaction and the water removed under reduced pressure giving a viscous residue. To this residue, 10 mL ethanol was added to dissolve it, then 2 mL of ether was added and a little impurity (white solid) was removed and the solvent removed under reduced pressure. The same process was repeated three times, and the pure liquid ligand was obtained (**L**). ^{1}H NMR (400 MHz, D_2O): δ 3.89 (4H, NCH_2CO_2), 3.45 (12H, CH_2NCH_2), 2.17 (2H, CH2C). MS *m*/*z*: 259.4 (M^+).

2.3.2. [CoLCl] (1). $CoCl_2 \cdot 6H_2O$ (0.237 g, 1.0 mmol) was added to an ethanol solution (10 mL, 1.0 mmol) containing **L**. The mixture was adjusted to pH 7 by NaOH (2 mol L^{-1}) and 3 drops of H_2O_2 (30%) were added. The solution was stirred for 0.5 h, filtered and allowed to stand in air at room temperature. After several weeks purple crystals suitable for X-ray measurements were obtained. The crystals were filtered and washed with cooled ethanol. Yield 48%. Anal. Calcd for $C_{11}H_{19}ClCoN_3O_4$(%): C, 37.54; H, 5.40; N, 11.94. Found: C, 37.85; H, 5.62; N, 11.70. IR spectrum (KBr; cm^{-1}): 3143[v (NH)], 1646[v_{as} (COO^-)], 1345[v_s (COO^-)].

2.3.3. $[FeLCl]_2 \cdot 3H_2O$ (2). The procedure was the same except that $FeCl_3$ (0.162 g, 1.0 mmol) was substituted for $CoCl_2 \cdot 6H_2O$. After a few days yellow crystals suitable for X-ray measurements were obtained. The crystals were filtered and washed with cooled ethanol. Yield 75%. Anal. Calcd for $C_{22}H_{44}N_6C_{12}Fe_2O_{11}$(%): C, 35.15; H, 5.85; N, 11.18. Found: C, 35.12; H, 5.21; N, 11.18. IR spectrum (KBr; cm^{-1}): 3406[v (H_2O)], 3166[v (NH)],1657[v_{as} (COO^-)], 1324[v_s (COO^-)].

2.4. *X-ray crystallography*

Diffraction data for **1** and **2** were collected on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 298 K. The structures were solved by direct methods and refined by full-matrix least-square on F^2 using the SHEXTL-97 crystallographic software package [23]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in calculated positions with fixed C–H and N–H distances (C–H, 0.97 Å; N–H, 0.89 Å). The hydrogen atom positions of the water molecules in the structure of **2** were refined with restraints. The crystallographic data for **1** and **2** are summarized in table 1. Select bond distances and angles were given in table 2.

3. Results and discussion

3.1. *Description of the structures*

The crystal structure of **1** is composed of neutral molecule of [CoLCl]. Figure 1(a) shows the ORTEP view of the molecule. There is a pseudo threefold axis, and the metal atom is situated on the threefold axis. The Co(III) is six-coordinate with three

Table 1. Crystal data and structure refinement for complexes **1** and **2**.

Complexes	**1**	**2**
CCDC deposit No.	CCDC-648010	CCDC-648011
Empirical formula	$C_{11}H_{19}Cl\ CoN_3O_4$	$C22H44Cl2Fe_2N_6O_11$
Formula weight	351.67	751.23
Crystal size (mm^3)	0.396 × 0.287 × 0.152	0.387 × 0.269 × 0.158
T (K)	298(2)	298(2)
Crystal system	Orthorhombic	Monoclinic
Space group	pbca	$C2/c$
Unit cell dimensions (Å, °)		
a	14.143(7)	26.5029(15)
b	11.917(6)	8.7155(4)
c	15.498(7)	28.6386(16)
α	90.00	90.00
β	90.00	110.7370(10)
γ	90.00	90.00
V (Å^3)	2612(2)	6186.6(6)
Z	8	8
Density ($g\,cm^{-1}$)	1.789	1.613
$F(000)$	1456	3136
Absorption coefficient (mm^{-1})	1.536	1.176
θ range for data collection (°)	1.55–25.10	1.52–25.05
Index ranges	$-16 \le h \le 11$, $-14 \le k \le 14$, $-18 \le l \le 18$	$-31 \le h \le 31$,$-10 \le k \le 8$, $-34 \le l \le 33$
Reflections collected/unique	11323($R_{int} = 0.0843$), 2318	15110($R_{int} = 0.0259$), 5474
Data/restraints/parameters	2318/0/184	5474/6/412
Goodness of fit (F^2)	1.039	1.055
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0633$; $wR_2 = 0.1698$	$R_1 = 0.0338$; $wR_2 = 0.0825$
R indices (all data)	$R_1 = 0.0744$; $wR_2 = 0.1885$	$R_1 = 0.0432$; $wR_2 = 0.0884$
Largest diff. peak and hole (e Å^{-3})	1.444 and −1.530	0.759 and −0.436

Table 2. Select bond distances (Å) and bond angles (°) for complexes **1** and **2**.

Complex **1**					
Co(1)–N(1)	1.983(3)	Co(1)–N(2)	1.952(3)	Co(1)–N(3)	1.955(3)
Co(1)–O(1)	1.920(3)	Co(1)–O(3)	1.925(3)	Co(1)–Cl(1)	2.2727(15)
N(2)–Co(1)–N(1)	99.36(13)	N(3)–Co(1)–N(1)	87.47(13)	N(2)–Co(1)–N(3)	84.90(13)
O(1)–Co(1)–O(3)	88.02(12)	O(1)–Co(1)–Cl(1)	91.53(7)	O(3)–Co(1)–Cl(1)	92.29(8)
O(3)–Co(1)–N(1)	170.63(12)	O(1)–Co(1)–N(2)	175.32(13)	N(3)–Co(1)–Cl(1)	177.90(9)
Complex **2**					
Fe(1)–N(1)	2.172(2)	Fe(1)–N(2)	2.148(2)	Fe(1)–N(3)	2.197(2)
Fe(1)–O(1)	1.9851(17)	Fe(1)–O(3)	1.9904(17)	Fe(1)–Cl(1)	2.2480(8)
Fe(2)–N(4)	2.178(2)	Fe(2)–N(5)	2.131(2)	Fe(2)–N(6)	2.191(2)
Fe(2)–O(5)	1.9805(18)	Fe(2)–O(7)	2.0034(18)	Fe(2)–Cl(2)	2.2495(7)
N(2)–Fe(1)–N(1)	81.07(8)	N(2)–Fe(1)–N(3)	86.78(8)	N(1)–Fe(1)–N(3)	82.37(8)
O(1)–Fe(1)–O(3)	89.91(8)	O(1)–Fe(1)–Cl(1)	97.75(6)	O(3)–Fe(1)–Cl(1)	99.42(6)
N(1)–Fe(1)–Cl(1)	172.50(6)	O(1)–Fe(1)–N(3)	157.98(8)	O(3)–Fe(1)–N(2)	162.71(8)
N(5)–Fe(2)–N(6)	88.15(8)	N(5)–Fe(2)–N(4)	81.60(10)	N(4)–Fe(2)–N(6)	81.70(9)
O(7)–Fe(2)–N(5)	163.97(8)	O(5)–Fe(2)–Cl(2)	98.38(6)	O(7)–Fe(2)–Cl(2)	98.12(6)
O(5)–Fe(2)–N(6)	158.08(8)	O(5)–Fe(2)–O(7)	90.66(8)	N(4)–Fe(2)–Cl(2)	174.22(7)

nitrogens and two oxygens of **L**, and the other coordination site is occupied by chloride, forming a distorted octahedral geometry. The degree of distortion from the regular prismatic or octahedral arrangement of the N_3O_2Cl donor set may be expressed by the twist angle, φ, defined in chart 1; φ is 0° for a prismatic and 30° for an octahedral arrangement [24].

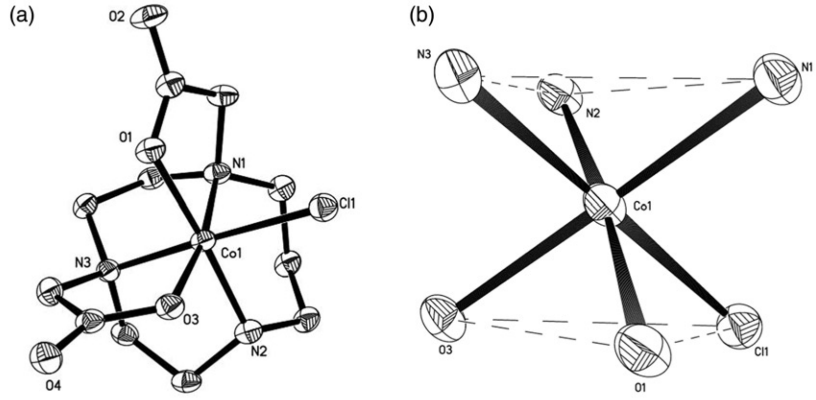


Figure 1. (a) ORTEP view of complex **1** with 30% thermal ellipsoid probability; (b) ORTEP view of the sandwich structure CoN$_3$O$_2$Cl core in complex **1**.

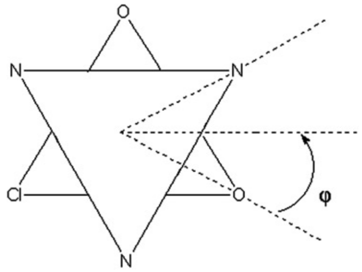


Chart 1. The twist angle definition.

In **1**, φ is 23.6°, indicating a distorted octahedral geometry, three nitrogens N(1), N(2), N(3) defined one face of the octahedron with N(2)–Co(1)–N(1) of 99.36(13)°, N(3)–Co(1)–N(1) of 87.47(13)°, N(2)–Co(1)–N(3) of 84.90(12)°, and O(1), O(3), Cl(1) compose the opposite face with O(1)–Co(1)–O(3) of 88.02(12)°, O(1)–Co(1)–Cl(1) of 91.53(7)°, O(3)–Co(1)–Cl(1) of 92.29(8)°, forming a sandwich structure [figure 1(b)]. The dihedral angle between the two planes is 3.39°. The average N–Co–N and O–Co–Cl(O) band angles are 90.58 (13)° and 90.67(9)°, respectively, nearing the ideal octahedral value of 90°. The Co–Cl bond length is 2.273(15) Å and the average Co–N and Co–O bond lengths are 1.963(3) Å and 1.923(3) Å, respectively. To our knowledge, a crystal structure of a Co(III) complex containing macrocyclic triamines with three or two acetate groups has not been previously reported. Comparing to the Co(III) complex of the hexadentate macrocycle 1,4,7-triazacyclononane with three 2-hydroxypropyl pendante groups, the average Co–N bond length of **1** is longer, but Co–O is shorter (the average Co–N bond length is 1.949(7) Å, the average Co–O bond length is 1.939(6) Å [10]), perhaps due to the influence of chloride.

The asymmetric unit in **2** consists of two neutral molecules of [LFeCl] and three lattice water molecules. The two crstallographically different neutral molecules have different dimensions, and, as a consequence, selected bond distances and angles for the two neutral molecules are all given in table 2. Figure 2 shows an ORTEP view of one of the two neutral molecules.

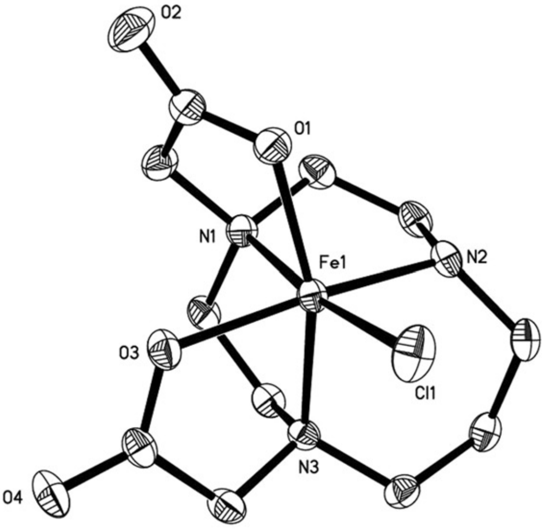


Figure 2. ORTEP view of one LFeCl individual.

It is clear from figure 2 that the coordination environment around the metal atom of **2** is similar to that of **1**. In **2**, φ is 12.8°, indicating the complex forms a distorted-prismatic environment rather than octahedral for the N_3O_2Cl donors. According to the literature [25], the macrocyclic ligand is expected to favor a trigonal-prismatic structure, especially when coordinated to a large metal ion, in order to minimize ligand strain energy. [LFeCl] is a high-spin complex, and therefore, no electronic preference of an octahedral environment over any other geometry is to be expected in terms of simple ligand field stabilization arguments. The same effect had been observed for a series of transition-metal complexes containing the hexadentate macrocycle ligand 1,4,7-triazacyclononane-N,N′,N″-triacetate (TCTA) [25, 26].

The Fe–Cl bond length is 2.248(8) Å, and the Fe–N bond lengths are in the range of 2.131(2) to 2.197(2) Å, with the shortest Fe(2)–N(5). The average Fe–O and Fe–N bond lengths are 1.987(17) Å and 2.173(2) Å, respectively, similar with the high-spin [Fe(TCTA)] complex (the average distances Fe–O = 1.962(2) Å and Fe–N = 2.181(3) Å) [26], but the Fe(2)–N(5) distance in **2** is the shortest. The reason may be lack of acetate on the N(5) atom and the influence of the hydrogen bond between N(5) and O(1).

Complex **2** has a two-dimensional framework structure through hydrogen bonds, as shown in figures 3(a) and (b). Hydrogen bonding parameters are listed in table 3. All the nitrogens and pendant oxygens of **L** and lattice water molecules take part in forming hydrogen bonds, and dimers are formed through two hydrogen bonds, N(2AA), O(1AA) and O(5AA), N(5AA), respectively [figure 3(a)]. Three adjacent water molecules (O10Z, O11Z, O9BZ) form a triatomic water cluster (O10Z $\cdots$ O11Z $\cdots$ O9BZ) through O $\cdots$ O $\cdots$ O hydrogen bond [O11 $\cdots$ $O10^{i}$, 2.846(5) Å, O11–H11A $\cdots$ $O10^{i}$, 164(4)°; O11 $\cdots$ $O9^{ii}$, 2.800(4) Å, O11–H11B $\cdots$ $O9^{ii}$, 165(5)°. Symmetry code: (i) $x, -y, z-1/2$; (ii) $-x, -y, -z+1$]. In addition, the other two O $\cdots$ O hydrogen bonds are formed through water molecule O(10Z), O(9BZ) and the adjacent uncoordinated pendant oxygen (O(8AA)) and O(4AF), respectively

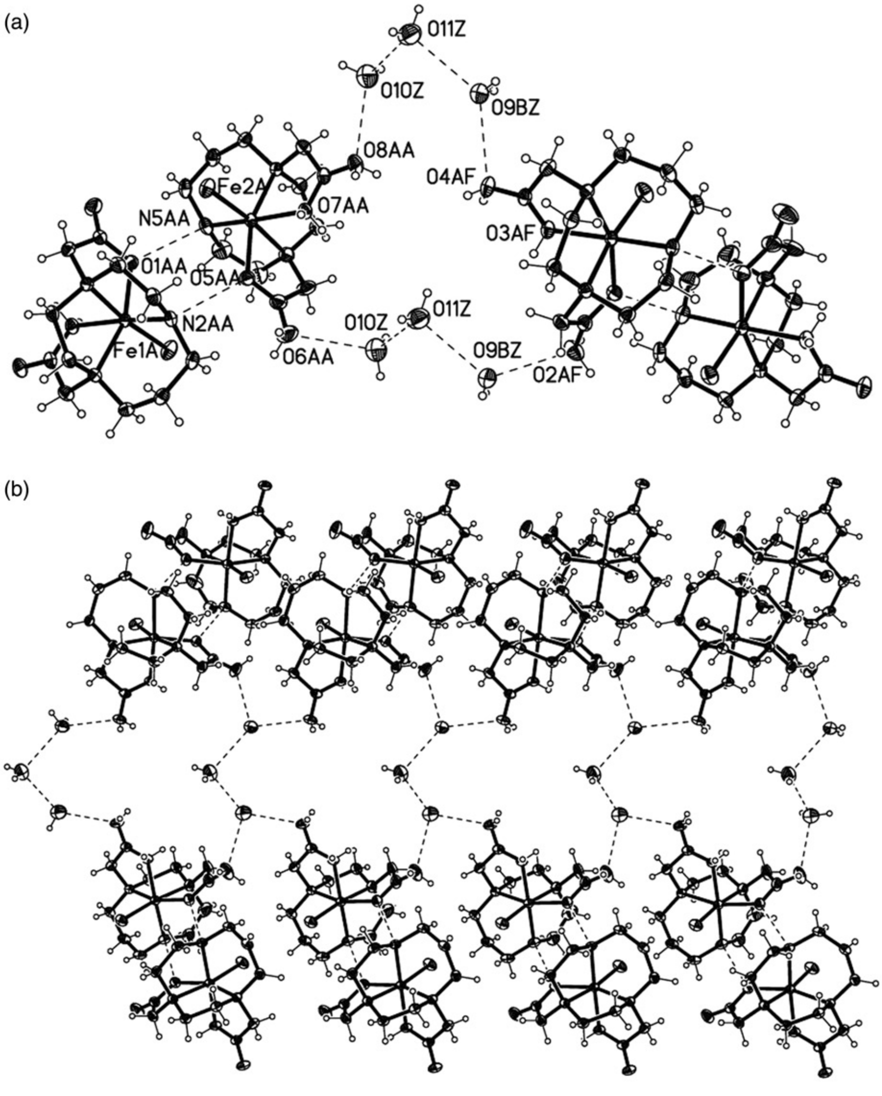


Figure 3. (a) View of the hydrogen bonds of complex **2;** (b) Space filling view of two-dimensional frameworks formed by hydrogen bonds along a axis.

[O10 $\cdots$ O8, 2.819(4) Å, O10–H10D $\cdots$ O8, 160(9)°; O9 $\cdots$ O4$^{\text{iii}}$, 2.872(3) Å, O9–H9C $\cdots$ O4$^{\text{iii}}$, 171(4)°. Symmetry code: (iii) $-x+1$, $-y+1$, $-z+2$]. Through these hydrogen bonds, a two-dimension supramolecular network with regular trigonal water cluster is formed [figure 3(b)].

3.2. *IR and UV–Vis spectra*

IR spectra of **1** and **2** display characteristic strong sharp peaks of **L** at 3143 and 3166 cm^{-1}, respectively, indicating N–H stretching. For **2**, a slightly broad band at 3406 cm^{-1} is attributed to the O–H stretching for lattice water. Strong bands at 1646

Table 3. Hydrogen Bonding Parameters[a] of complex **2**.

D–H $\cdots$ A	D–H (Å)	H $\cdots$ A (Å)	D $\cdots$ A (Å)	∠D–H $\cdots$ A (°)
O11–H11A $\cdots$ O10^{i}	1.000(10)	1.873(16)	2.846(5)	164(4)
011–H11B $\cdots$ 09^{ii}	1.004(10)	1.818(18)	2.800(4)	165(5)
O9–H9C $\cdots$ O4^{iii}	0.988(10)	1.893(13)	2.872(3)	171(4)
O10–H10D $\cdots$ 08	1.001(11)	1.86(4)	2.819(4)	160(9)
O10–H10C $\cdots$ O6^{iv}	0.998(10)	1.883(14)	2.872(4)	171(4)
O9–H9D $\cdots$ O2^{v}	0.987(10)	1.809(11)	2.795(3)	179(4)
N2–H2 $\cdots$ O5^{vi}	0.83(3)	2.22(3)	3.018(3)	161(2)
N5–H5 $\cdots$ O1^{vii}	0.83(3)	2.16(3)	2.972(3)	164(3)

[a] Symmetry code: (i) $x, -y, z-1/2$; (ii) $-x, -y, -z+1$; (iii) $-x+1, -y+1, -z+2$; (iv) $x, y-1, z$; (v) $-x+1, -y, -z+2$; (vi) $x+1/2, y-1/2, z$; (vii) $x-1/2, y+1/2, z$.

(for **1**), and 1657 cm^{-1} (for **2**) could be traced to υ_{asym}(carboxyl), and at 1345 for **1**, 1362 cm^{-1} for **2** to the υ_{sym}(carboxyl). The frequency differences ($\triangle$) between υ_{asym}(carboxyl) and υ_{sym}(carboxyl) are 301 for **1** and 295 cm^{-1} for **2**, respectively, larger than 200 cm^{-1}, indicating a monodentate acetate [27]. These spectral assignments are confirmed by single crystal X-ray diffraction analysis.

The ultraviolet and visible spectra measured in the 200–800 nm range for **1** and **2** in water show absorbances at 259 and 279 nm, attributed to charge transfer and transition of the ligand itself, respectively. For **1**, two medium bands at 371 nm and 529 nm and one weak band at 739 nm are tentatively attributed to $^1A_{1g} \rightarrow {}^1T_{2g}$, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^3T_{2g}$, respectively, for Co in an octahedral field [28]. For **2**, the shoulder band at 313 nm is tentatively assigned to the charge-transfer transitions of Fe(III) center from the nitrogen groups to the metal d orbital. The absorption has also been observed in (1,4,7-triazacyclonanane) iron(III) complex [29].

3.3. *Thermal decomposition*

The thermal behaviors of **1** and **2** were studied from 25 to 800°C under nitrogen (figure 4). The TGA curves indicate similar weight-loss. For **1**, there is a stable platform between 25 and 300°C, then the ligand and chloride are lost from 300 to 520°C (the lost weight is 48.51%, calculated value is 49.29%). The final residue is Co_2O_3 identified by XPRD, with yield of 23.60% (calculated value is 23.05%). For **2**, the first step loses three lattice water molecules (the lost weight is 7.88%, calculated value is 7.22%) in the 40–100°C temperature range. The second step loses the ligand and chloride between 250°C and 620°C (the lost weight is 72.95%, calculated value is 71.58%). The final residue is Fe_2O_3 also confirmed by XPRD. (The residue value is 19.98%, calculated value is 21.2%.)

Supplementary materials

Tables with atomic coordinates, bond distances, bond angles and thermal parameters for all atoms including hydrogen atoms, may be obtained from the authors on request. Crystallographic data for the structure of the complexes **1** and **2** have been deposited in

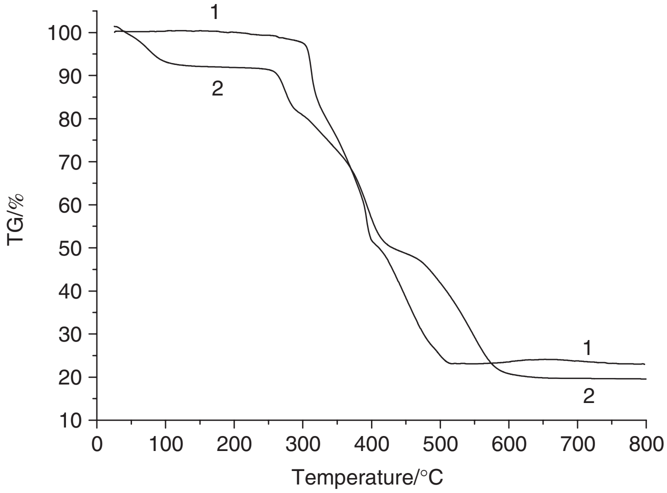


Figure 4. TGA curves of complex **1** and **2**.

the Cambridge Crystallographic Data Centre as supplementary No. CCDC-648010 & 648011, respectively.

Acknowledgments

This work was supported by grants from the National Natural Science foundation of China and Shaanxi Natural Science Foundation (No. 2002B04).

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