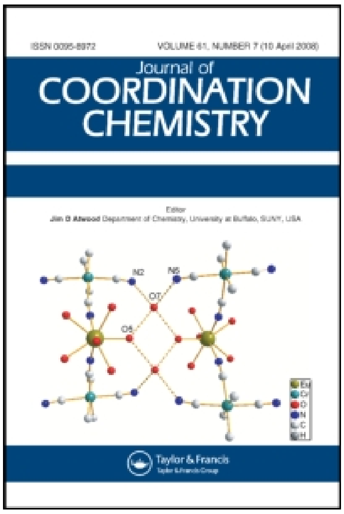

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Synthesis and structures of two cobalt complexes $[NaCo^{II}(NTA)(H_2O)]_{<i>n</i>}$ and $NH_4[Co^{III}(IDA)_2] \cdot 2H_2O$

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Synthesis and structures of two cobalt complexes $[NaCo^{II}(NTA)(H_2O)]_n$ and $NH_4[Co^{III}(IDA)_2]\cdot 2H_2O$

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Two cobalt complexes $[NaCo^{II}(nta)(H_2O)]_n$ (H_3nta = nitrilotriacetic acid) (**1**) and $NH_4[Co^{III}(ida)_2]\cdot 2H_2O$ (H_2ida = iminodiacetic acid) (**2**) have been synthesized and characterized by single-crystal X-ray diffraction analysis. Compound **1** crystallizes in the orthorhombic system, space group $P2_12_12_1$ with $a = 7.9770(12)$ Å, $b = 9.7613(15)$ Å, $c = 12.1945(18)$ Å, $V = 949.5(2)$ Å^3, $Z = 4$, and $R_1 = 0.0705$ for 1597 observed reflections. Compound **2** crystallizes in the monoclinic system, space group $P2(1)/c$ with $a = 5.1801(3)$ Å, $b = 11.2073(6)$ Å, $c = 12.2891(7)$ Å, $V = 707.09(7)$ Å^3, $Z = 2$, and $R_1 = 0.0349$ for 1143 observed reflections. In compound **1**, the Co is coordinated by a nitrogen and five oxygen atoms in a distorted octahedral geometry $\{CoNO_5\}$, and the Na is coordinated by one water molecule and four carboxyl oxygen atoms in slightly distorted square pyramidal geometry. The entire structure shows a three-dimensional network. In compound **2**, Co atom is equatorially coordinated by two ida ligands in a distorted octahedral geometry $\{CoN_2O_4\}$. The discrete $[Co(ida)_2]^{2-}$ anions are linked by hydrogen bonding to a three-dimensional supramolecular network.

Keywords: Cobalt; Nitrilotriacetic acid; Iminodiacetic acid; Crystal structure

1. Introduction

As members of the carboxylate ligands containing N-donors, nitrilotriacetate (nta) or iminodiacetate (ida) can act as potential bifunctional ligands with variable multidentate coordination modes. A series of nta [1–3] and ida [4–9] complexes have been isolated and structurally characterized. In previous reports, we described the synthesis and crystal structures of several nta [10–12] and ida [13, 14] complexes. As a part of our continuing investigation on this type of complex, we herein present the crystal structures of two new cobalt complexes $[NaCo^{II}(nta)(H_2O)]_n$ (**1**) and $NH_4[Co^{III}(ida)_2]\cdot 2H_2O$ (**2**).

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2. Experimental

Elemental analysis was performed with a Vario EL *III* CHNOS Elemental Analyzer. IR spectra of KBr pellets were recorded in the range of 4000–400 cm^{-1} on an FTS-40 spectrophotometer. UV-visible spectra were recorded in aqueous solution with a Perkin-Elmer Model L 19 spectrophotometer.

2.1. *Preparation of* $[NaCo^{II}(nta)(H_2O)]_n$ *(1)*

A mixture of H_3nta (0.9 mmol), $Co(CH_3COO)_2 \cdot 4H_2O$ (0.5 mmol) and H_2O (20 mL) was stirred for about 30 min, and then NaOH solution (0.5 N) was added to adjust the pH to 5–6. Three weeks later, purple crystals were obtained. Analysis Calcd for $C_6H_8NO_7CoNa$: C, 25.02; H, 2.80; N, 4.86%. Found: C, 25.07; H, 2.76; N, 4.81%. IR (KBr pellet, cm^{-1}): 3514 (s), 3361 (s), 1630 (s), 1583 (s), 1431 (s), 1392 (s), 1323 (m), 1296 (m), 1128 (m), 951 (w), 926 (m), 908 (m), 748 (m), 629 (m), 553 (w). Yield: 57%.

2.2. *Preparation of* $NH_4[Co^{III}(ida)_2] \cdot 2H_2O$ *(2)*

A mixture of H_2ida (0.6 mmol), Co_2O_3 (0.5 mmol), NH_4VO_3(1.2 mmol) and H_2O (25 mL) was stirred and refluxed for about 30 min, and then NaOH solution (0.5 N) was added to adjust pH value to 3–4. Two weeks later, purple crystals were obtained. Analysis Calcd for $C_8H_{20}N_4O_9Co$: C, 25.61; H, 4.84; N, 11.20%. Found: C, 25.57; H, 4.79; N, 11.24%. IR (KBr pellet, cm^{-1}): 3645 (s), 3415 (s), 3120 (s), 1660 (s), 1367 (s), 1333 (m), 1238 (w), 1117 (s), 1045 (s), 962 (w), 926 (m), 903 (m), 785 (m), 611 (w), 573 (w), 536 (m), 459 (w). Yield: 23%.

2.3. *X-ray crystallography*

Crystals with dimensions $0.28 \times 0.21 \times 0.06\,mm^3$ for **1** and $0.31 \times 0.26 \times 0.07\,mm^3$ for **2** were mounted on a computer-controlled Siemens SMART CCD diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. The structures were solved by direct methods, successive Fourier difference synthesis and refined by full matrix least-squares based on F^2 using the SHELXTL-97 program package. All non-hydrogen atoms were refined anistropically. In **1**, H atoms bound to C atoms were placed in calculated positions, while H atoms of water molecule were located in the difference Fourier map. In **2**, H atoms of organic ligand were generated geometrically and refined as riding, while other H atoms were not located. The crystallographic data are listed in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

A locally expanded unit of compound **1** is shown in figure 1, displaying the coordination environments of Na and Co atoms. Co(II) atom is coordinated by a nitrogen atom and five oxygen atoms in a distorted octahedral geometry $\{CoNO_5\}$. Of the five oxygen atoms, three (O1, O3, O5) are from one nta ligand while the others (O2A, O6A) are

Table 1. Crystallographic parameters for $[NaCo^{II}(nta)(H_2O)]_n$ (**1**) and $NH_4[Co^{III}(ida)_2] \cdot 2H_2O$ (**2**).

Empirical formula	$C_6H_8CoNNaO_7$ (**1**)	$C_8H_{18}CoN_3O_{10}$ (**2**)
Molecular weight	288.05	375.18
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
a (Å)	7.9770(12)	5.1801(3)
b (Å)	9.7613(15)	11.2073(6)
c (Å)	12.1945(18)	12.2891(7)
β (°)		97.649(2)
V (Å^3)	949.5(2)	707.09(7)
Z	4	2
T (K)	293(2)	293(2)
D_c (g cm^{-3})	2.015	1.762
F (000)	580	388
μ (mm^{-1})	1.873	1.272
λ (Å)	0.71073	0.71073
Goodness of fit on F^2	1.252	1.108
Largest diff. Peak and hole (e Å^{-3})	1.152 and −0.811	0.469 and −0.403
Final R indices $[I > 2\sigma(I)]$[a]	$R_1 = 0.0705$	$R_1 = 0.0349$
	$wR_2 = 0.1518$	$wR_2 = 0.0962$
R indices (all data)	$R_1 = 0.0751$	$R_1 = 0.0382$
	$wR_2 = 0.1551$	$wR_2 = 0.0993$

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$.

Table 2. Selected bond lengths (Å) and angles (°) for $[NaCo^{II}(nta)(H_2O)]_n$ (**1**) and $NH_4[Co^{III}(ida)_2] \cdot 2H_2O$ (**2**).

$C_6H_8CoNNaO_7$ (**1**)			
N(1)–Co(1)	2.139(8)	Co(1)–O(1)	2.119(7)
Co(1)–O(6)#1	2.047(7)	Co(1)–O(2)#2	2.130(7)
Co(1)–O(3)	2.050(7)	Co(1)–O(5)	2.129(7)
O(6)#1–Co(1)–O(3)	89.2(3)	O(1)–Co(1)–O(5)	157.1(3)
O(6)#1–Co(1)–O(1)	114.4(3)	O(2)#2–Co(1)–O(5)	83.9(3)
O(3)–Co(1)–O(1)	91.6(3)	O(6)#1–Co(1)–N(1)	164.7(3)
O(6)#1–Co(1)–O(2)#2	90.9(3)	O(3)–Co(1)–N(1)	82.6(3)
O(3)–Co(1)–O(2)#2	176.8(3)	O(1)–Co(1)–N(1)	78.9(3)
O(1)–Co(1)–O(2)#2	91.3(3)	O(2)#2–Co(1)–N(1)	96.5(3)
O(6)#1–Co(1)–O(5)	88.1(3)	O(5)–Co(1)–N(1)	79.5(3)
O(3)–Co(1)–O(5)	92.9(3)	Co(1)–N(1)	1.931(2)
$C_8H_{18}CoN_3O_{10}$ (**2**)	1.882(2)	O(1)#1–Co(1)–N(1)	93.04(9)
Co(1)–O(3)	1.888(2)	O(3)–Co(1)–N(1)#1	92.98(8)
Co(1)–O(1)	90.21(9)	O(3)#1–Co(1)–N(1)#1	87.02(8)
O(3)–Co(1)–O(1)	89.79(9)	O(1)–Co(1)–N(1)#1	93.04(9)
O(3)–Co(1)–O(1)#1	90.21(9)	O(1)#1–Co(1)–N(1)#1	86.96(9)
O(3)#1–Co(1)–O(1)#1	87.02(8)		
O(3)–Co(1)–N(1)	92.98(8)		
O(3)#1–Co(1)–N(1)	86.96(9)		
O(1)–Co(1)–N(1)			

(**1**) Symmetry transformations used to generate equivalent atoms: #1 $-x+2$, $y-1/2$, $-z+3/2$; #2 $x+1/2$, $-y+1/2$, $-z+2$.

(**2**) Symmetry transformations used to generate equivalent atoms: #1 $-x+3$, $-y$, $-z+1$.

from two nta ligands. The Co–O distances are in the range 2.047(7)–2.130(7) Å and the Co–N distance is 2.139(8) Å, comparable to the corresponding values found in other Co^{II} nta complexes [15–17]. This Na atom is coordinated by five oxygen atoms in which one (O7) is from a water molecule with Na–O distance of 2.280(10) Å while the others are from four carboxylate groups with Na–O distances of 2.248(9)–2.445(7) Å,

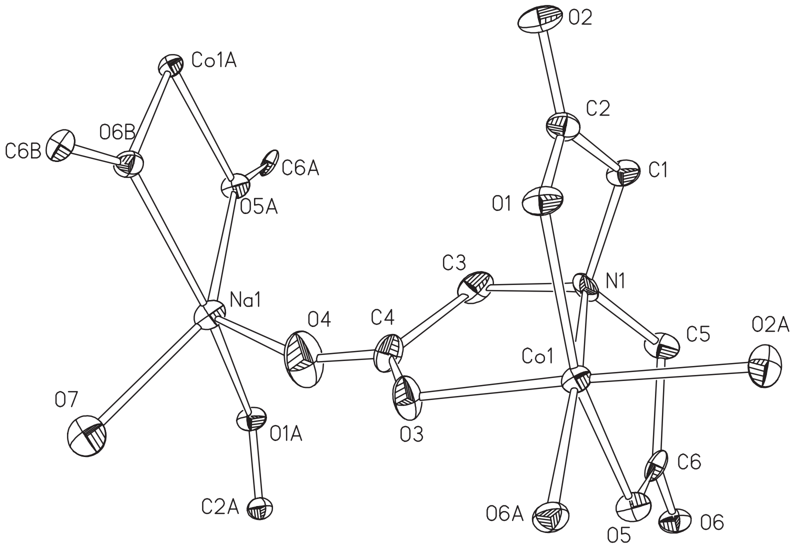

Figure 1. A locally expanded unit of compound **1**, showing the coordination environments of metal atoms with 30% thermal ellipsoids.

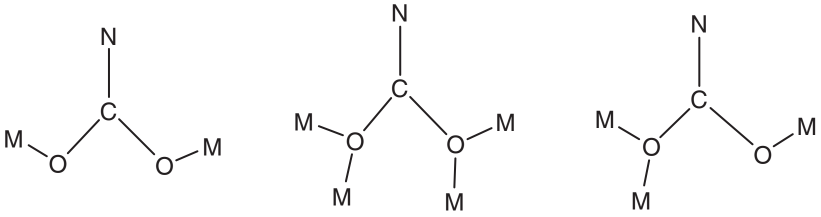

Figure 2. The coordination modes of carboxyl groups of nta ligand.

forming a slightly distorted square pyramid $\{NaO_5\}$. The apical position of the pyramid is occupied by a carboxyl oxygen atom (O4) with Na–O distance of 2.248(9) Å, while the equatorial plane is defined by O7, O1A, O5A and O6A atoms with mean deviation of ca 0.194 Å. The Na atom is linked to Co atoms through three ways: O1 as bridge; O5 and O6 as bridge; and O–C–O group as bridge, with corresponding Na···Co distances of 3.42, 3.83 and 6.16 Å. The nta ligand is ten-coordinate. Three carboxylate groups exhibit different coordination environments (figure 2), connecting two, three or four metal atoms via their carboxyl oxygen atoms. As far as we are aware, this type of coordination mode of nta has not been previously reported. The O–C–O bond angles are 124.7(9), 125.1(10) and 123.7(9)°.

In the crystal structure of **1**, each Co links the other four Co atoms via four carboxylate bridges in two *syn*-*anti* and two *anti*-*anti* modes, with Co···Co distances of 5.37–6.02 Å. As shown in figure 3, six Co atoms are linked by the carboxylate groups to produce an elliptic ring (**A**) with the farthest Co···Co distance of 12.590(2) Å. The rings are connected to form an interesting two-dimensional layer. The layers are further linked by Co atoms along the *a*-axis to form a three-dimensional network. Especially, the space of **A** is occupied by two square pyramids of $\{NaO_5\}$,

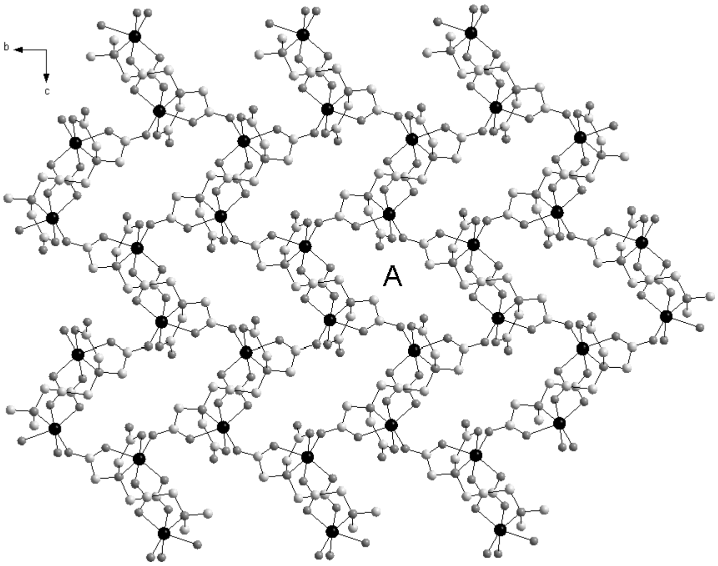

Figure 3. The two-dimensional layer of **1**.

which further stabilize the three-dimensional structure. To date, although a large number of nta complexes of transition metals have been reported, few exhibit three-dimensional networks [18, 19].

The molecular structure of **2** is shown in figure 4. The Co(III) is equatorially coordinated to two ida ligands through their two nitrogen and four oxygen atoms with a distorted octahedral geometry $\{CoN_2O_4\}$. The two ida ligands are linked through the Co atom in a typical *fac*-chelating arrangement with two nitrogen atoms in *trans* positions. The Co–N bond length is 1.931(2) Å, while Co–O1 and Co–O3 distances are both 1.888(2) Å. As expected, the values are comparable to those in other Co(III) iminodiacetates [20–22]. The ida ligand is tridentate; two oxygen atoms (O1, O3) from two carboxyl groups and one nitrogen atom are bound to Co atom. In either chelating ring Co–O1–C1–C2–N1 or Co–O3–C3–C4–N1, all the atoms are coplanar with mean deviation of 0.0867 and 0.0926 Å. The dihedral angle between the two chelating rings is 77.1°, and the C1–O1, C1–O2, C3–O3 and C3–O4 distances are 1.296(4), 1.225(4), 1.295(3) and 1.226(3) Å, respectively.

Hydrogen bonding exists in both complexes. Three weak interactions involved in **1** are $C1–H1A\cdots O1^{i}$ (symmetry code: (i) $-0.5+x,\ 0.5-y,\ 2-z$), $O7–H7A\cdots O2^{ii}$ (symmetry code: (ii) $1-x,\ 0.5+y,\ 1.5-z$) and $O7–H7A\cdots O3^{iii}$ symmetry code: (iii) $-0.5+x,\ 0.5-y,\ 1-z$) with the corresponding distances of 3.38(1), 2.90(1) and 2.80(1) Å, respectively. The crystal structure of **2** is also stabilized by hydrogen bonding. As shown in figure 5, two adjacent $[Co(ida)_2]^-$ anions are linked via two weak $C–H\cdots O$ and $N–H\cdots O$ interactions. An anionic chain is formed along the *a*-axis through two weak intermolecular interactions, with the $C4–H4B\cdots O4^{iv}$ and $N1–H1A\cdots O3^{iv}$ (symmetry code: (iv) $x+1,\ y,\ z$) distances of 2.920(3) and 3.270(4) Å, respectively (table 3). Furthermore, free ammonium ions and water molecules ($C4–H4A\cdots O5$)

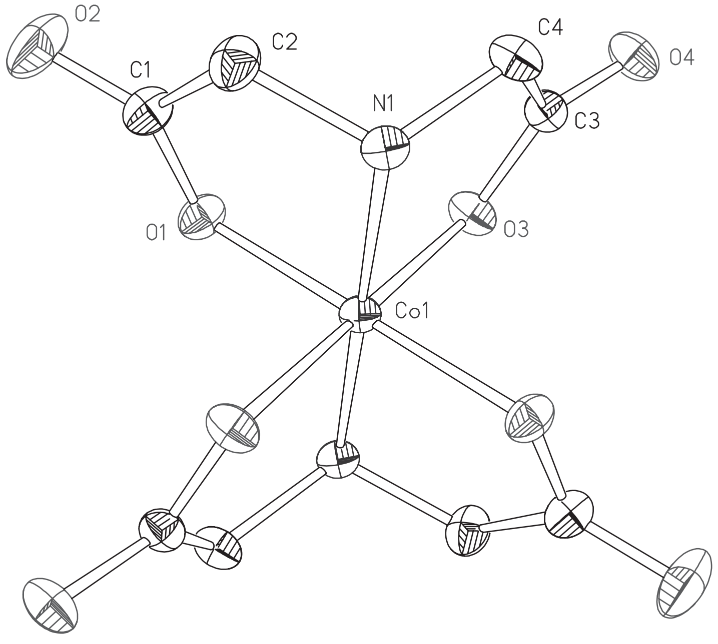

Figure 4. Molecular structure of **2** showing the atom-labeling scheme and 30% thermal ellipsoids. Ammonium ion and water molecules are omitted.

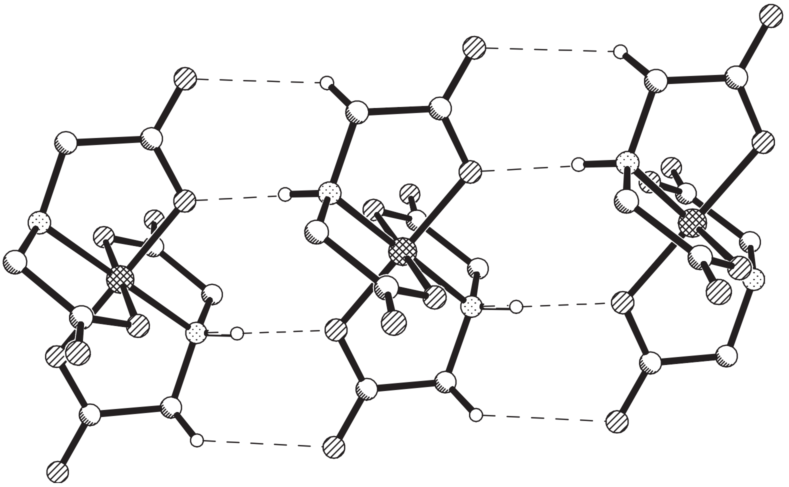

Figure 5. The hydrogen bonding formed between adjacent $[Co(ida)_2]^-$ anions.

are hydrogen bonded to the anionic chains and further link the chains to a three-dimensional supramolecular structure (figure 6).

IR spectra show that the stretching modes ν(OH) of water and ν(N–H) of ammonium ion are in the range of 3645–3120 cm^{-1} for the compounds. The value of ν(C–N) in **1** is 1128 cm^{-1} while in **2** it is 1117 cm^{-1}, indicating the nitrogen atoms of the ligands are coordinated to the metal atoms. The ν_{as}(COOH) of **1** red-shifts to 1630 cm^{-1} while **2** red-shifts to 1660 cm^{-1}, suggesting the carboxyl groups in the compounds are

Table 3. Hydrogen bonding geometry (Å°).

D–H···A	D–H	H···A	D···A	D–H···A
N(1)–H(1A)···O(3)#1	0.91	2.01	2.920(3)	173.5
C(4)–H(4B)···O(4)#1	0.97	2.56	3.270(4)	130.5
C(4)–H(4A)···O(5)	0.97	2.57	3.293(4)	131.1

Symmetry transformations used to generate equivalent atoms, #1: $x+1$, y, z.

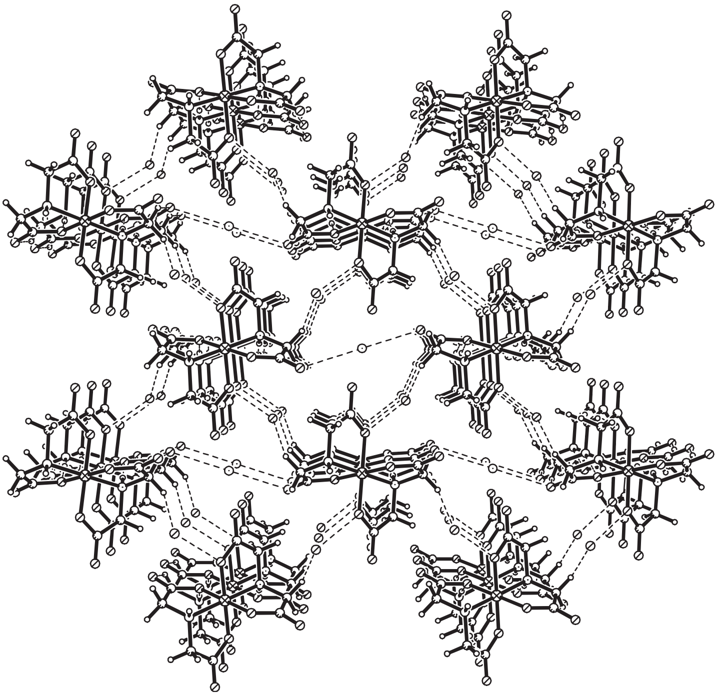

Figure 6. The packing diagram of **2**, showing the three-dimensional network viewed along the *a*-axis.

bound to the metal centers. The UV-vis spectrum of **1** in aqueous solution shows a broad band centered at 515 nm, which could be ascribed to d–d transitions, as in octahedral Co(II) compound [23]. Compound **2** displays two distinct bands at 365 and 500 nm and a weak band at 620 nm. The first could be assigned to ligand-to-metal charge transitions while the latter two bands could be ascribed to $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ electron transitions of the octahedrally coordinated Co(III) [14, 24].

Supplementary material

CCDC-265802 for **1** and CCDC-267615 for **2** contain the supplementary crystallographic data for this article. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax; (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

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