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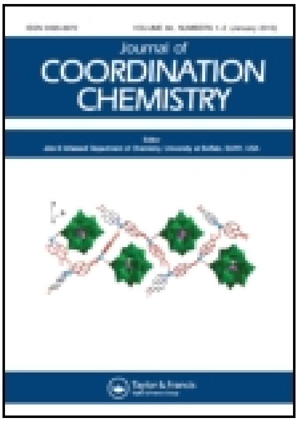

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Solvothermal syntheses and structures of three clusters based on (1H-benzoimidazol-2-yl)-methanethiol

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Accepted author version posted online: 12 Mar 2013.Published online: 15 Apr 2013.

To cite this article: Jing Jing Guo , Wei Wang , Yi Dong Zhang , Li Yang , Shu Hua Zhang & Xiu Qing Zhang (2013) Solvothermal syntheses and structures of three clusters based on (1H-benzoimidazol-2-yl)-methanethiol, Journal of Coordination Chemistry, 66:8, 1467-1476, DOI: 10.1080/00958972.2013.783907

To link to this article: http://dx.doi.org/10.1080/00958972.2013.783907

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Journal of Coordination Chemistry, 2013
Vol. 66, No. 8, 1467–1476, http://dx.doi.org/10.1080/00958972.2013.783907

Solvothermal syntheses and structures of three clusters based on (1H-benzoimidazol-2-yl)-methanethiol

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(*Received 27 May 2012; in final form 4 January 2013*)

Two hexanuclear cobalt clusters $[Co_6(bms)_{12}]\cdot(X)_6\cdot yH_2O$ (1, $X = NO_3^-$, $y = 12$; **2**, $X = ClO_4^-$, $y = 8$) and one new trinuclear nickel cluster $[Ni_3S(bms)_3]\cdot NO_3\cdot C_2H_5OH$ (**3**) (Hbms = (1H-benzoimidazol-2-yl)-methanethiol) have been synthesized and characterized by elemental analysis, IR spectrum, and X-ray single-crystal diffraction. Compound **1** crystallizes in the trigonal system, $R\overline{3}$ space group, and consists of hexanuclear Co^{III} units, which are bridged by μ_2-S-benzimidazoles in a square arrangement around cobalt. Compound **2** crystallizes in the monoclinic system, $P2_1/n$ space group, and also consists of hexanuclear Co^{III} units containing the same kind of μ_2-S-benzimidazole bridges like **1**, but contains different counter anions and lattice waters. Compound **3** crystallizes in the orthorhombic system, *Pbca* space group, and is composed of trinuclear Ni^{II} units. These results show that geometries and sizes of the corresponding anions as well as their coordinating mode and hydrogen-bonding properties are important in determining the final structures of the assemblies.

Keywords: Crystal structure; Water cluster; Polynuclear cluster

1. Introduction

Attentions have been paid towards self-assembly of metallasupramolecular species, and numerous discrete molecular architectures with different shapes and functionalities have been synthesized to approach the goal of prediction and design [1, 2]. Interest in polymetallic clusters of paramagnetic transition metal ions has increased since the discovery of “single-molecule magnets” [3, 4]. An effective and facile approach for the synthesis of such complexes is an appropriate choice of well-designed organic ligands as bridges or terminal groups with metal ions, or metal clusters as nodes. (1H-Benzoimidazol-2-yl)-methanethiol (Hbms) may construct various structures with interesting magnetic properties for the following reasons: (1) The bms anion possesses two nitrogens of benzimidazole and one sulfur of thiol and might be utilized as a linker in constructing interesting coordination polymers, (2) The thiol group also displays a variety of bonding geometries, such as μ-S [5], μ_2-S [6], μ_3-S [7], and μ_4-S [8], and (3) Complexes constructed by

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(1H-benzoimidazol-2-yl)-methanol (Hbm is similar to Hbms) formed multinuclear clusters [9, 10]. Previous investigations implied that cobalt complexes constructed by Hbm derivatives may form polymetallic clusters and favor ferromagnetic coupling through μ_3-O-bridges and towards SMM behavior [9]. Therefore, Hbms may form multinuclear clusters. Relatively small modification in the bridging ligand may change the overall structures of the assembly [11]. Hbms may provide unpredictable and interesting polymetallic clusters different from Hbm because the coordination mode of the thiol of Hbms is different from that of methanol of Hbm, which will have a profound impact on electron density of such a ligand and therefore, different physical and chemical properties. However, polymetallic clusters of Hbms with transition metals have not been reported.

To further understand coordination chemistry of Hbms and prepare new materials with interesting polymetallic clusters and physical properties, herein, we report synthesis and crystal structures of two cobalt polymetallic clusters $[Co_6(bms)_{12}]\cdot(X)_6\cdot yH_2O$ (**1**, $X = NO_3^-$, $y = 12$; **2**, $X = ClO_4^-$, $y = 8$) and one new trinuclear nickel cluster $[Ni_3S(bms)_3]\cdot NO_3\cdot$-$C_2H_5OH$ (**3**).

2. Experimental

2.1. *Materials and physical measurements*

All reagents were commercially available and used without purification. The C, H, N microanalyses were carried out with a PE 2400 series II elemental analyzer. FT-IR spectra were recorded from KBr pellets from 4000 to 400 cm^{-1} on a PE spectrum one FT-IR spectrometer. The crystal structures were determined by a Bruker Smart Apex CCD diffractometer and SHELXL crystallographic software.

2.2. *Solvothermal syntheses*

2.2.1. Preparation of 1. A mixture of $Co(NO_3)_2\cdot 6H_2O$ (0.291 g, 1 mM), Hbms (0.165 g, 1 mM), and ethanol (8 mL) with pH of 7.5 by the addition of triethylamine was put into a Teflon-lined autoclave (15 mL) and heated at 140 °C for 3 days. Red needles of **1** were collected by filtration, washed with ethanol and dried in air. Phase pure crystals of **1** were obtained by manual separation (yield: 142.4 mg, *ca*. 58.9% based on Hbms). Anal. Calcd for **1**: $C_{96}H_{108}Co_6N_{30}O_{30}S_{12}$ (Mr = 2900.42), Calcd: C, 39.75; H, 3.75; N, 14.48%. Found: C, 39.72; H, 3.79; N, 14.52%.

2.2.2. Preparation of 2. **2** can be prepared in a similar way to **1** except that $Co(ClO_4)_2\cdot 6H_2O$ was used instead of $Co(NO_3)_2\cdot 6H_2O$. Red needles of **2** were collected by filtration, washed with ethanol, and dried in air. Phase pure crystals of **2** were obtained by manual separation (yield: 82.3 mg, *ca*. 32.35% based on Hbms). Anal. Calcd for **2**: $C_{96}H_{100}Cl_6Co_6N_{24}O_{32}S_{12}$ (Mr = 3053.00), Calcd: C, 37.76; H, 3.30; N, 11.01%; Found: C, 37.72; H, 3.35; N, 11.06%.

2.2.3. Preparation of 3. **3** can be prepared in a similar way to **1** except that $Ni(NO_3)_2\cdot 6H_2O$ was used instead of $Co(NO_3)_2\cdot 6H_2O$. Green block crystals of **3** were collected by filtration, washed with ethanol, and dried in air. Phase pure crystals of **3** were obtained by manual separation (yield: 94.5 mg, *ca*. 46.9% based on Hbms). Anal. Calcd for **3**: $C_{26}H_{27}N_7Ni_3O_4S_4$ ($Mr = 805.90$), Calcd: C, 38.75; H, 3.38; N, 12.17%; Found: C, 38.69; H, 3.42; N, 12.12%. IR data for **3** (KBr, cm^{-1}): 3424(s), 1623(w), 1384(s), 1100 (m), 746(m) (s, strong; m, medium; w, weak).

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive.

2.3. *Structural determination*

Diffraction data were collected on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo-Ka radiation ($\lambda = 0.71073$ Å) at 296 K using the ω–θ scan mode in the range $2.32 \leqslant \theta \leqslant 25.10°$ (**1**), $2.32 \leqslant \theta \leqslant 25.01°$ (**2**) and $2.48 \leqslant \theta \leqslant 25.10°$ (**3**). Raw frame data were integrated with the SAINT program. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on F^2 using SHELXS-97 [12]. The empirical absorption corrections were applied with SADABS [12]. All non-hydrogen atoms were refined anisotropically. All hydrogens were positioned geometrically and refined by a riding mode. Calculations and graphics were performed with SHELXTL [12]. The crystallographic details are provided in table 1, while the selected bond distances and angles for **1–3** are listed in tables 2–4. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center. CCDC reference numbers for **1–3** are 883123–883125, respectively.

Table 1. Crystallographic and experimental data for **1–3**.

Compound	**1**	**2**	**3**
Molecular formula	$C_{96}H_{108}Co_6N_{30}O_{30}S_{12}$	$C_{96}H_{100}Cl_6Co_6N_{24}O_{32}S_{12}$	$C_{26}H_{27}N_7Ni_3O_4S_4$
Molecular weight	2900.42	3053.00	805.90
T [K]	293(2)	293(2)	293(2)
Crystal system	Trigonal	Monoclinic	Orthorhombic
Space group	$R\overline{3}$	$P2_1/n$	$Pbca$
a [å]	30.420(3)	19.374(2)	10.6651(17)
b [å]	30.420(3)	12.4206(15)	22.950(4)
c [å]	11.288(2)	24.927(3)	25.629(4)
β [°]	90	94.247(2)	90
V [Å^3]	9046(2)	5981.9(13)	6273.0(18)
Z	3	2	8
D_{calcd} [g cm^{-3}]	1.597	1.695	1.715
μ [mm^{-1}]	1.100	1.243	2.094
θ range [°]	2.32 to 25.10	2.32 to 25.01	2.50 to 25.10
R_{int}	0.1063	0.1028	0.0824
Parameters	262	797	398
GOF	1.019	1.048	1.092
$F(0\ 0\ 0)$	4464	3112	3296
R_1 [$I \geqslant 2\sigma(I)$]$^{a,\ b}$	0.0556	0.0709	0.0432
wR_2 (all data)$^{a,\ b}$	0.1640	0.2273	0.1049
Residues [eÅ^{-3}]	0.569 and −0.481	0.888 and −0.973	0.599 and −0.388

Notes: $^{a}R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$;
^{b} $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w(|F_o^2|)^2]^{1/2}$.

Table 2. Selected bond lengths [Å] and angles [°] for **1**.

Co1–N3	1.972(5)	Co1–S1$^{\mathrm{i}}$	2.2466(17)
Co1–N1	2.003(5)	Co1–S2	2.2615(18)
Co1–S1	2.2424 (17)	Co1–S2$^{\mathrm{ii}}$	2.2782(18)
Co1–Co1a	3.374(1)	S1···S1A	3.082(1)
S1···S1C	3.485(1)	S1···S1E	4.652(1)
S1–Co1–S1$^{\mathrm{i}}$	86.74(8)	N1–Co1–S1$^{\mathrm{i}}$	169.92(16)
N1–Co1–S2	90.03(15)	S1–Co1–S2	91.59(6)
N1–Co1–S2$^{\mathrm{ii}}$	96.90(15)	S1–Co1–S2$^{\mathrm{ii}}$	82.90(6)
N3–Co1–N1	92.8(2)	S1$^{\mathrm{i}}$–Co1–S2	83.18(6)
N3–Co1–S1	177.70(16)	S1$^{\mathrm{i}}$–Co1–S2$^{\mathrm{ii}}$	89.14(6)
N3–Co1–S1$^{\mathrm{i}}$	94.23(14)	S2–Co1–S2$^{\mathrm{ii}}$	170.80(8)
N3–Co1–S2	86.46(15)	Co1–S2–Co1$^{\mathrm{i}}$	96.02(6)
N3–Co1–S2$^{\mathrm{ii}}$	99.20(15)	Co1–S1–Co1$^{\mathrm{ii}}$	97.46(6)
N1–Co1–S1	86.01(16)		

Symmetry codes: (i) $x-y+1$, $x+1$, $-z+1$; (ii) $y-1$, $-x+y$, $-z+1$.

Table 3. Selected bond lengths [Å] and angles [°] for **2**.

Co1–N3	1.959(7)	Co2–S2	2.258(3)
Co1–N1	1.988(6)	Co2–S3	2.271(2)
Co1–S6$^{\mathrm{i}}$	2.239(2)	Co2–S5	2.282(2)
Co1–S2	2.247(2)	Co3–N9	1.967(8)
Co1–S1	2.277(3)	Co3–N11	1.991(6)
Co1–S3	2.284(3)	Co3–S6	2.243(2)
Co2–N5	1.962(7)	Co3–S4	2.259(2)
Co2–N7	2.000(7)	Co3–S5	2.261(3)
Co2–S4	2.246(3)	Co3–S1$^{\mathrm{i}}$	2.272(3)
N1–Co1–S1	85.5(2)	S3–Co2–S5	169.77(10)
N1–Co1–S2	176.0(2)	S4–Co2–S2	87.50(9)
N1–Co1–S3	101.1(2)	S4–Co2–S3	91.27(8)
N1–Co1–S6$^{\mathrm{i}}$	95.6(2)	S4–Co2–S5	82.82(8)
N3–Co1–N1	92.5(3)	N9–Co3–N11	92.0(3)
N3–Co1–S1	90.0(2)	N9–Co3–S6	176.7(2)
N3–Co1–S2	85.6(2)	N9–Co3–S4	94.8(2)
N3–Co1–S3	97.3(2)	N9–Co3–S5	87.2(2)
N3–Co1–S6$^{\mathrm{i}}$	169.1(2)	N9–Co3–S1$^{\mathrm{i}}$	99.3(2)
S1–Co1–S3	169.89(9)	N11–Co3–S4	170.5(2)
S2–Co1–S3	82.70(8)	N11–Co3–S5	90.7(2)
S2–Co1–S1	90.87(9)	N11–Co3–S6	85.8(2)
S6$^{\mathrm{i}}$–Co1–S1	83.44(9)	N11–Co3–S1$^{\mathrm{i}}$	98.0(2)
S6$^{\mathrm{i}}$–Co1–S2	85.78(8)	S4–Co3–S5	83.00(8)
S6$^{\mathrm{i}}$–Co1–S3	88.31(9)	S4–Co3–S1$^{\mathrm{i}}$	87.48(9)
N5–Co2–N7	90.9(3)	S5–Co3–S1$^{\mathrm{i}}$	168.90(9)
N5–Co2–S4	175.8(2)	S6–Co3–S4	87.14(8)
N5–Co2–S2	95.5(2)	S6–Co3–S5	90.38(9)
N5–Co2–S3	86.2(2)	S6–Co3–S1$^{\mathrm{i}}$	83.45(9)
N5–Co2–S5	100.2(2)	Co3$^{\mathrm{i}}$–S1–Co1	95.23(9)
N7–Co2–S2	171.0(2)	Co1–S2–Co2	97.63(9)
N7–Co2–S3	91.4(2)	Co2–S3–Co1	96.19(9)
N7–Co2–S4	85.8(2)	Co3–S5–Co2	96.38(9)
N7–Co2–S5	96.5(2)	Co2–S4–Co3	97.45(9)
S2–Co2–S3	82.74(8)	Co1$^{\mathrm{i}}$–S6–Co3	97.13(9)
S2–Co2–S5	88.64(9)		

Symmetry code: (i) $-x+1$, $-y+1$, $-z+1$.

Table 4. Selected bond lengths [Å] and angles [°] for **3**.

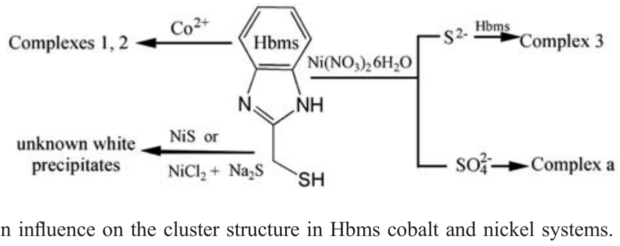
Ni1–S4	2.1699(13)	Ni2–S1	2.2211(14)
Ni1–S1	2.1913(14)	Ni2–N3	1.914(4)
Ni1–S3	2.2310(14)	Ni3–S3	2.1853(14)
Ni1–N1	1.889(4)	Ni3–S4	2.1876(14)
Ni2–S4	2.1861(14)	Ni3–S2	2.2129(14)
Ni2–S2	2.1887(15)	Ni3–N5	1.917(4)
Ni1···Ni2	2.772(5)	Ni1···Ni3	2.777(5)
Ni2···Ni3	2.771(5)	Ni2–S4–Ni3	78.64(4)
N1–Ni1–S1	88.08(13)	N5–Ni3–S2	104.98(12)
N1–Ni1–S3	104.47(13)	N5–Ni3–S3	88.95(12)
N1–Ni1–S4	171.66(13)	N5–Ni3–S4	169.74(13)
S1–Ni1–S3	161.78(5)	S3–Ni3–S2	161.98(6)
S4–Ni1–S1	84.23(5)	S3–Ni3–S4	82.97(5)
S4–Ni1–S3	82.31(5)	S4–Ni3–S2	81.80(5)
N3–Ni2–S1	104.68(13)	Ni1–S1–Ni2	77.84(5)
N3–Ni2–S2	88.95(14)	Ni2–S2–Ni3	78.04(5)
N3–Ni2–S4	170.72(14)	Ni3–S3–Ni1	77.92(5)
S2–Ni2–S1	161.96(6)	Ni1–S4–Ni2	79.05(5)
S4–Ni2–S1	83.15(5)	Ni1–S4–Ni3	79.18(4)
S4–Ni2–S2	82.39(5)		

3. Results and discussion

3.1. *Synthesis*

The reaction between Hbm and Co^{2+} has been previously shown to yield Co_4, Co_7, and Co_{12} clusters [9, 10]. Herein, bm adopts two coordinating modes: one is $\mu_2:\eta^1:\eta^2$, the other is $\mu_2:\eta^1:\eta^3$. In order to study the role of bm in the formation of the metal-assemblies, Hbms is the same structure as Hbm, but thiol was used instead of methanol of Hbm. Reactions of three different salts ($Co(NO_3)_2{\cdot}6H_2O$ for **1**, $Co(ClO_4)_2{\cdot}6H_2O$ for **2,** and $Ni(NO_3)_2{\cdot}6H_2O$ for **3**) and Hbms were investigated in our work. Discrete hexanuclear and trinuclear clusters of **1–3** in reasonable yield and high purity were generated by reactions in the presence of triethylamine in ethanol solution. Herein, the thiol is the most important parameter in the formation of **1–3**. The size of the coordination atom may influence the structures of those clusters. The van der Waals radii of oxygen and sulfur are 1.4 and 1.85 Å, respectively, perhaps, causing the difference in coordination between Hbm and Hbms.

For **3**, S^{2-} was synthesized by an *in situ* disproportionation. The C–S bond of bms was cleaved forming SO_4^{2-} and S^{2-}. In the process of synthesizing **3**, crystals of $NiSO_4{\cdot}6H_2O$ (**a**) [13] were generated confirming the disproportionation reaction. To determine the specific source of sulfide, direct reactions of NiS or $NiCl_2{\cdot}4H_2O$, and Na_2S with Hbms in ethanol under the same hydrothermal conditions were carried out. Complex **3** cannot be obtained, only an unknown white precipitates (Scheme 1), confirming that sulfide comes from Hbms not from metal salt.



Scheme 1. Metal ion influence on the cluster structure in Hbms cobalt and nickel systems.

3.2. *Structural descriptions*

3.2.1. Complexes 1 and 2. The structures of **1** and **2** are similar, (see figure 1, figure S1, and tables 1–3) except counter anions and lattice water. Therefore, only **1** is analyzed here.

Single-crystal X-ray diffraction analysis reveals that **1** belongs to a trigonal space group $R\overline{3}$ with bar-3 symmetry. Complex **1** consists of a ring-like hexanuclear cationic cluster $[Co_6(bms)_{12}]^{6+}$, 12 waters and six NO_3^- which lie at a site with threefold symmetry (figure 1). The valences for six cobalts can be determined by the bond valence model [14]. According to this model, the sum of all bond valences around any ion is equal to its ionic charge or valence. Here, bond valences (s) are calculated as $s = \exp[(r_0 - r)/B]$; $B = 0.37$, $r_0 = 2.02$ for Co(III)-S pairs, $r_0 = 1.75$ for Co(III)–N pairs [15]. The calculated results are listed in table 5. The calculated values of bond valence are in agreement with the values of expected atomic valence, which indicates that all cobalt cations have a valence of + 3. Although topologically analogous $\{Co^{II}{}_6\}$ [16], $\{Mn^{II}{}_6\}$ [17], $\{Ni^{II}{}_6\}$ [18] and $\{Cu^{II}{}_6\}$ [7c, 19] complexes are known, **1** represents the first $\{Co^{III}{}_6\}$ complex to possess a planar hexagonal ring-like structure. All Co^{III} ions are coordinated by two N and four S from four bms ligands, forming a distorted octahedral geometry (*cis*-angles range from 82.90(6) to 96.90(15)°, *trans*-angles from 169.9(2) to 177.7(2)°). Co–N bond lengths are 1.97(5) and 2.003(5) Å, which are similar to the values observed in cobalt(III) complexes [20, 21], but obviously shorter than Co(II)–N average bond lengths in cobalt(II) complexes [22]. The core of the cluster is almost planar [plane equation: 11.288 $z = 5.6440$, Co1 and the centrosymmetric equivalents, deviation from the average plane 0.0319 Å]. The 12 bms anionic ligands (singly deprotonated at thiol site) bridge the peripheral Co^{III} centers adopting a $\mu_2:\eta^1:\eta^2$ coordination motif which is different from bm ligands [9, 10], lyingalternately above and below the $\{Co^{III}{}_6\}$ plane. In the cluster, adjacent Co···Co distance is 3.374 Å, which is slightly longer than 3.17–3.22 Å in $[Co_7(bzp)_6(N_3)_9(CH_3O)_3]\cdot(ClO_4)_2\cdot 2H_2O$ [23]. Compound **1** has a ring which shows approximate ring dimensions of

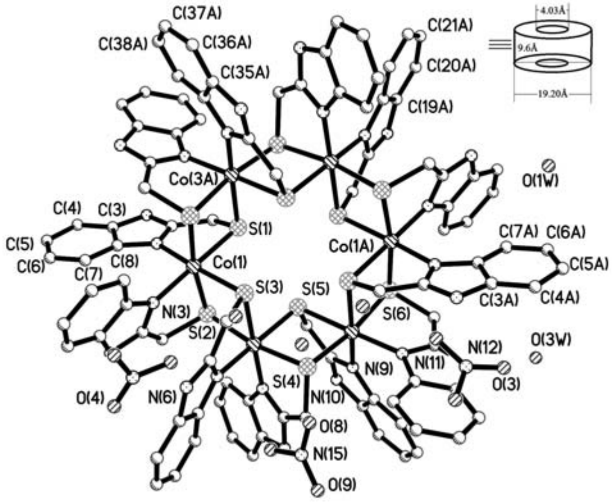


Figure 1. Ring-like cation structure of **1**. Hydrogens were omitted.

Table 5. Coordination number (N), bond valence sum (BVS), expected atomic valence (V) and deviation from the expected atomic valence (ΔV) for cobalt cations.

	1	2		
	Co1	Co1	Co2	Co3
N	6	6	6	6
BVS	3.04	3.08	3.04	3.07
V	+3	+3	+3	+3
ΔV	0.04	0.08	0.04	0.07

19.20 × 4.03 × 9.60 Å (outside × inside diameter × depth). Compound **1** further constructed a 1-D chain through hydrogen bonds along the z axis (figure 2). A hexa-member water ring exists between two $[Co_6(bms)_{12}]^{6+}$ along the z axis, further linking six nitrates through O–H⋯O hydrogen bonds (O2 W⋯O3, 2.501(17) Å, table S1, figure 3). The $[Co_7(bms)_{12}]^{n+}$ cluster which is similar to $[Co_7(bm)_{12}]^{2+}$ (Hbm = (1H-benzimidazol)-ethanol) is not formed [10]. The structure of the wheel-like cationic heptanuclear cluster $[Co_7(bm)_{12}]^{2+}$ is very similar to the ring-like cationic hexanuclear cluster $[Co_6(bms)_{12}]^{6+}$ (figure S2). The only difference is that the center of **1** does not contain cobalt, while the center of $[Co_7(bm)_{12}]^{2+}$ has one cobalt. Plane-like hexa-member water ring linking six nitrates may block the center position. Cobalt would be very comfortable in the position if it can enter and the Co–S bond should be 2.32 Å (figure 3).

3.2.2. Complex 3. Complex **3** crystallizes in the orthorhombic space group *Pbca* (figure 4). The core of the molecule contains three Ni^{II} ions arranged in an equilateral triangle bridged by three μ_2-S (thiol group, Ni1–S1–Ni2, 77.84(5)°; and Ni2–S2–Ni3, 78.04(5)°; Ni3–S3–Ni1, 77.92(5)°) with an Ni⋯Ni distance from 2.771 to 2.777 Å, which is shorter than that of $[Ni_3(N_3)_3(O_2CMe)_3(py)_5]$ (py = pyridine) [24] and $[Ni_3(mimp)_5(CH_3CN)]ClO_4$ (Hmimp is 2-methyliminomethylphenolate) [25]. This may be due to the smaller bond angles (table 4). Coordination of the nickels is completed by one nitrogen and two sulfurs of two bms and one terminal S^{2-}. All the three nickel ions are four-coordinate with distorted planar geometries. S^{2-} was synthesized by an *in situ* disproportionation through cleavage of C–S of bms, forming SO_4^{2-} and S^{2-}. In the process of synthesizing **3**, crystals of $NiSO_4{\cdot}6H_2O$ (**a**) were generated [13]. All three nickel ions are 2+, as evidenced by

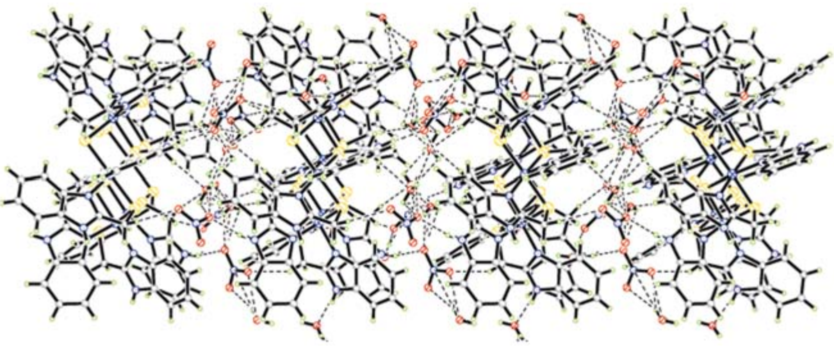


Figure 2. 1-D chain of **1**.

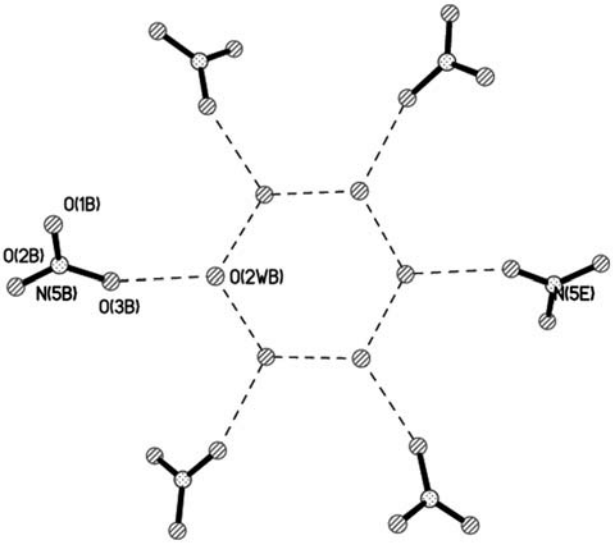


Figure 3. Relationship between six-member water cluster and nitrates in **1**.

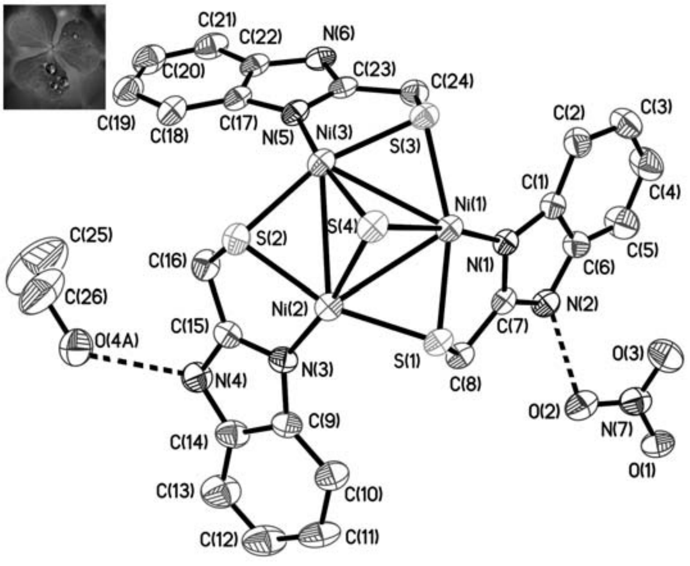


Figure 4. Shamrock-like trinuclear structure of **3**.

bond valence sum calculations [26], charge-balance considerations, and the presence of typical bond lengths for Ni^{II} (table 4). The complex formed a shamrock-like trinuclear cluster with the three bms like the three leaves of the shamrock, S^{2-} is the grass stalk and water and nitrate hang like dew on the shamrock (figure 4). Complex **3** further formed a 3-D network through N–H···O and O–H···O hydrogen bonds (table S2).

4. Conclusions

Three clusters have been synthesized from solvothermal method and their single-crystal structures were determined. The thiol in the synthesis seems to be the most important parameter in the formation of **1–3**. In the process of synthesizing **3**, the C–S bond of bms was cleaved forming SO_4^{2-} and S^{2-} ions.

Supplementary material

CCDC 883123–883125 for **1–3** contain the Supplementary crystallographic data for this article. Copies of the data can be obtained free of charge via the internet at http://www.ccdc.cam.ac.uk/conts/retrieving.html, or by post at CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223336033, E-mail: deposit@ccdc.cam.ac.uk). The structure of **2**. The contrast of the structures between $[Co_7(bm)_{12}]^{2+}$ and $[Co_6(bms)_{12}]^{6+}$. The structure of **a**. Hydrogen bonds of **1** and **3**.

Acknowledgments

This research was supported by National Natural Science Foundation of China (No. 21161006), Innovation Project of Guangxi Graduate Education (2010105960817M03), Startup foundation for Dr Zhang of Guilin University of Technology and Program for Excellent Talents in Guangxi Higher Education Institutions (Gui Jiao Ren [2012]41).

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[13] **a** can be prepared in the process of synthesizing **3** and green crystals were collected by filtration, washed with ethanol and dried in air, the phase pure **a** was obtained by manual separation, but the yield is very low. Crystal data for complex **a**: $H_{12}NiO_{10}S$, Mr = 262.87 g M^{-1} Tetragonal, $P4_12_12$, $a = b = 6.8100(5)$, $c = 18.355(3)$ Å, $V = 851.24(15)$ Å^3, $\theta = 28.20°$, $\lambda = 0.71073$ Å, μ(Mo Kα) = 2.554 mm^{-1}, 5083 reflections were collected of which 1051 were unique ($R_{\text{int}} = 0.0177$). The structure was solved by direct methods and refined by full-matrix least-squares of F^2, $R_1 = 0.0147(I > 2\sigma(I))$, $wR_2 = 0.0376$ (all data). Max/min residual electron density 0.176 / –0.258 e Å^3 and the structure of **a** see figure S3.

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