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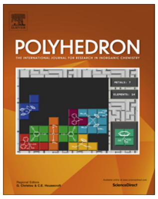

Structures and magnetism of {Ni_3}, {Ni_9}, {Ni_5} and {Ni_{12}} mercapto-tetrazole based clusters

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ABSTRACT

Four polynuclear mercaptotetrazole-based nickel clusters, $[Ni_3(hmt)_6(H_2O)_6]\cdot 4H_2O$ (**1**), $[(C_2H_5)_4N]_2[Ni_9(\mu_3\text{-}CH_3O)_8(hmt)_{12}]$ (**2**), $[Ni_5(\mu_3\text{-}OH)_2(Hdmt)_6(SCN)_8]$ (**3**), and $[Ni_{12}(\mu_6\text{-}CO_3)(\mu_3\text{-}CH_3O)_{12}(CH_3CO_2)_3(et)_6(H_2O)_{12}]\cdot Br\cdot 2H_2O$ (**4**), (here, Hhmt = 1-(2-hydroxyethyl)-5-mercapto-tetrazole, Hdmt = 1-[2-(N,N-dimethylamino)ethyl]-5-mercapto-tetrazole, Het = 5-(ethylthio)-1H-tetrazole), have been synthesized and characterized by elemental analysis, IR, powder X-ray diffraction and X-ray single-crystal diffraction. **1** shows a centrosymmetric linear trinuclear nickel cluster. **2** reveals of a dumbbell-like {Ni_9} cluster with S3 symmetry containing two $[Ni_4(CH_3O)_4]$ cubanes linked with a Ni atom through six "—N—N—" bridges. **3** reveals of a {Ni_5} cluster with a bowtie-like skeleton supported by μ_3-OH^- ions. **4** exhibits a plane- symmetry {Ni_{12}} cluster with an approximate trefoil shape based on three $[Ni_4(CH_3O)_4]$ cubanes bridged by a μ_6-CO_3^{2-}. The results show that the minor ligand modification accompanying the regulating of reaction conditions (anion, solvent, pH, temperature and the different ratios) have a key role in the structural control of the self-assembly process. Magnetic properties of **1**, **2** and **4** in the 2–300 K have also been discussed. The linear {Ni_3} (**1**) core displays dominant anti-ferromagnetic interactions from the nature of the binding modes through "—N—N—" bridges. The {Ni_9} (**2**) and {Ni_{12}} (**4**) clusters display dominant ferromagnetic interactions from the nature of the binding modes through μ_3-CH_3O^- and "—N—N—" bridges.

1. Introduction

Polynuclear clusters of paramagnetic metal ions have been attracting elicit research interest owing to their potential applications in areas of high density data storage, [1] magnetic refrigeration, [2] qubits for quantum computation, [3] and molecular spintronics, [4] and so on. Among them, Ni^{II} clusters have been receiving increasing attention in the field of molecular magnetism. [5] This $3d^8$ ion has shown promise in the synthesis of both single-molecule magnets (SMMs) [6] and spin-phonon traps, [7] with the former taking advantage of its significant single-ion anisotropy and the latter of its paramagnetic nature when confined with a highly symmetric cluster.

Much methodology for the design and synthesis of such clusters has been achieved significant progress. [8,9] An effective approach is still the appropriate choice of well-designed organic ligands. [10] 5-mercaptotetrazole derivatives ($R1\text{-}(SCN_4)\text{-}R2$, Scheme 1a) possessing four heterocyclic nitrogen atoms, have been demonstrated to be a good bridging group, with the soft sulfhydryl group having empty *3d* orbits to accept electrons from metal centers. [11] Our groups also reported a series of Cd^{II}/Cu^{I} compounds including some clusters based on Hdmt ligand (Scheme 1c) previously. [12] So, through introducing some small groups (eg. hydroxyethyl, 2-(N, N-dimethylamino)ethyl, ethyl), the modification to 5-mercaptotetrazole perhaps benefit the formation of different polymetallic clusters. While, to our knowledge, the systematic discussion for clusters based on such ligands are very limited. Besides, a modern trend is the employment of additional small anion ligands (such as N_3^-, CO_3^-, CH_3O^-, SCN^-, ClO_4^-, halogen ions and so on) in the reaction systems. [13] Because of that the loss of a degree of synthetic control is more than compensated for by the vast diversity of structural types using a combination of ligands. [14]

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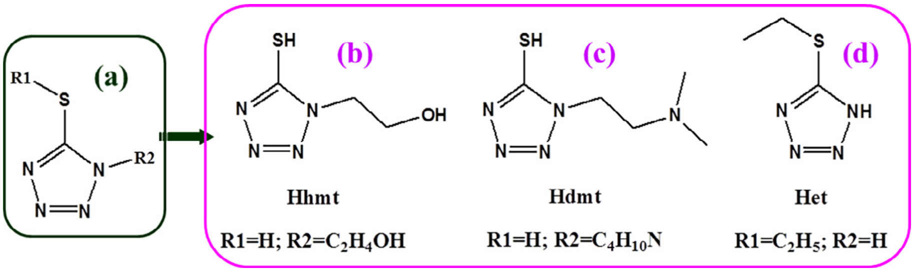

Scheme 1. The three ligands (b, Hhmt; c, Hdmt; d, Het) used in the work modified from the deuterogenic 5-mercaptotetrazole ligand (a, R1-(SCN_4)-R2).

Based on the consideration above, four novel Ni(II) polymetallic clusters named $[Ni_3(hmt)_6(H_2O)_6]\cdot 4H_2O$ (**1**), $[(C_2H_5)_4N]_2[Ni_9(\mu_3\text{-}CH_3O)_8(hmt)_{12}]$ (**2**), $[Ni_5(\mu_3\text{-}OH)_2(Hdmt)_6(SCN)_8]$ (**3**) and $[Ni_{12}(\mu_6\text{-}CO_3)(\mu_3\text{-}CH_3O)_{12}(CH_3CO_2)_3(et)_6(H_2O)_{12}]\cdot Br\cdot 2H_2O$ (**4**) were constructed successfully in this paper. With the modification of the R1-(SCN_4)-R2 ligand (Scheme 1), accompanying the additional of small anions and the regulation of the metal–ligand ratio and temperature, clusters of **1**–**4** reveal different skeletons based on $\{Ni_3\}$ linear, $\{Ni_9\}$ dumbbell containing two $[Ni_4(CH_3O)_4]$ cubanes, $\{Ni_5\}$ bowtie consisting of two co-vertex triangles, and $\{Ni_{12}\}$ trefoil containing three $[Ni_4(CH_3O)_4]$ cubanes, respectively. Variable-temperature magnetic susceptibility measurement of the complexes reveal the existence of dominant anti-ferromagnetic interactions with in **1** and ferromagnetic interactions in **2**, **4** respectively.

2. Experimental

2.1. Materials and physical measurements

All the chemicals were commercial products without further purification. Elemental analyses for C, H, N and S were performed on a PerkinElmer 2400II elemental analyzer. The IR spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer with KBr pellets in the range 400–4000 cm^{-1}. The magnetic susceptibility measurements were measured on polycrystalline samples with a Quantum Design MPMS-XL7 SQUID magnetometer using an applied magnetic field of 1000 Oe over the temperature range of 2–300 K. A diamagnetic correction to the observed susceptibilities was applied using Pascal's constants. X-ray powder diffraction (XRPD) intensities were measured on a Rigaku D/max-IIIA diffractometer (Cu Kα, λ = 1.54056 Å). The single crystalline powder samples were prepared by crushing the crystals and scanned from 3 to 60° with a step of 0.1°/s. Calculated patterns of **1**–**4** were generated with PowderCell.

Caution! Metal complexes with tetrazole organic ligands are potentially explosive.

2.2. Synthesis of complexes **1**–**4**

2.2.1. $[Ni_3(hmt)_6(H_2O)_6]\cdot 4H_2O$ (**1**)

A mixture of Hhmt (87.6 mg, 0.6 mmol), $Ni(OAc)_2\cdot 4H_2O$ (74.66 mg, 0.3 mmol), methanol (10 mL) and $CHCl_3$ (0.5 mL) was stirred under refluxing for 5 h at 65 °C. Then cooled and filtrated. The filtrate was allowed to slowly concentrate by evaporation at room temperature. 40 days later, green block crystals were obtained in *ca.*50 % yield. *Anal.* Calc. for $C_{18}H_{50}N_{24}Ni_3O_{16}S_6$: C, 17.62; H, 4.11; N, 27.39; S, 15.68. Found: C, 17.03; H, 4.32; N, 27.75; S, 15.74%. IR (KBr, cm^{-1}): 3190m, 2346w, 1621m, 1389s, 1317s, 1240w, 1201s, 1141m, 1054s, 1012w, 952s, 856m, 683m.

2.2.2. $[(C_2H_5)_4N]_2[Ni_9(\mu_3\text{-}CH_3O)_8(hmt)_{12}]$ (**2**)

A mixture of Hhmt (0.3 mmol), $Ni(OAc)_2\cdot 4H_2O$ (74.66 mg, 0.3 mmol), methanol (10 mL) and triethylamine (1 mL) was put into a Teflon-lined autoclave (23 mL) and then heated at 120 °C for 3 days. The cool solution yielded brown block single crystals in *ca.*55 % yield. *Anal.* Calc. for $C_{60}H_{124}N_{50}Ni_9O_{20}S_{12}$: C, 25.93; H, 4.50; N, 25.20; S, 13.85. Found: C, 25.65; H, 4.71; N, 24.99; S, 13.69%. IR (KBr, cm^{-1}): 3566w, 3435m, 2924m, 2822m, 1656w, 1639m, 1472s, 1433s, 1396s, 1323s, 1293s, 1202m, 1128m, 1075s, 1043s, 701w, 680w.

2.2.3. $[Ni_5(\mu_3\text{-}OH)_2(Hdmt)_6(SCN)_8]$ (**3**)

Hdmt (34.65 mg, 0.20 mmol), $Ni(OAc)_2\cdot 4H_2O$ (74.66 mg, 0.3 mmol), KSCN (38.87 mg, 0.40 mmol), water (5 mL) and ethanol (5 mL) were stirred under refluxing for 4 h at 60 °C and then cooled and filtered. About 60 days later, a few green needlelike crystals were obtained. Yield: 5 %. *Anal.* Calc. for $C_{38}H_{68}N_{38}Ni_5O_2S_{14}$: C, 24.92; H, 3.74; N, 29.06; S, 24.51. Found: C, 24.05; H, 3.58; N, 29.37; S, 24.18%. IR (KBr, cm^{-1}): 3392m, 3019m, 2719m, 2091s, 2021s, 1624w, 1459s, 1410s, 1382s, 1328s, 1180w, 1102w, 1034w, 905w, 774w.

2.2.4. $[Ni_{12}(\mu_6\text{-}CO_3)(\mu_3\text{-}CH_3O)_{12}(CH_3CO_2)_3(et)_6(H_2O)_{12}]\cdot Br\cdot 2H_2O$ (**4**)

A mixture of Het (39.0 mg, 0.3 mmol), Na_2CO_3 (105.9 mg, 1 mmol), $Ni(OAc)_2\cdot 4H_2O$ (149.2 mg, 0.6 mmol), KBr (35.7 mg, 0.3 mmol), methanol (10 mL) and $CHCl_3$ (0.5 mL) was stirred under refluxing for 5 h at 65 °C. 20 days later, green block crystals were obtained in *ca.* 45% yield. *Anal.* Calc. for $C_{37}H_{103}N_{24}Ni_{12}O_{35}S_6Br$: C, 18.35; H, 4.29; N, 13.89; S, 7.95. Found: C, 18.04; H, 4.08; N, 14.10; S, 8.13%. IR (KBr, cm^{-1}): 3325m, 1567s, 1404s, 1353s, 1262s, 1042s, 680w, 617w, 458w.

2.3. Crystal structure determination

X-ray single-crystal diffraction data for **1**–**4** were recorded on a Agilent SuperNova apparatus at 298 K by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The primitive structures were solved by the direct method and refined by full-matrix least-squares techniques on F^2 using SHLXTL-97 program. [15] Further crystallographic data and structural refinement details are summarized in Table 1. Selected bond lengths and angles are listed in Table S1. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center. CCDC reference numbers: 1448957–1448960 (**1**–**4**).

3. Results and discussion

3.1. Structure discussion of the complexes

3.1.1. [Ni3(hmt)6(H2O)6]·4H2O (**1**)

Single-crystal X-ray crystallographic analysis of compound **1** reveals a linear trinuclear Ni(II) cluster (Fig. 1), in which Ni1 atom is located on a crystallographic symcenter and is coordinated octahedrally by six tetrazole N atoms from different hmt ligands with Ni1–N bond lengths range from 2.045(3) to 2.117(3) Å (Table S1). Ni1 is bridged to Ni2 through three "—N—N—" bridges from three