

In situ amination and side group effect of multifunctional heterocyclic thione ligand toward discrete and polymeric cluster construction†

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Three metal complexes $[\text{Cu}_6(\text{atdm})_6]$ (**1**), $[\text{Cu}^{\text{I}}(\text{Hatd})(\text{H}_2\text{atd})]$ (**2**) and $[\text{H}_3\text{O}][\text{Co}_4^{\text{III}}\text{Co}_2^{\text{III}}\text{Cl}_3(\text{atd})_6]\cdot\text{H}_2\text{O}$ (**3**) [atdm = 4-dimethylamino-6-anilino-1,3,5-triazine-2-thiolate, H_2atd = 6-anilino-1,3,5-triazine-2,4-dithiol, atdH_2 = 6-anilino-1,3,5-triazine-2,4(1*H*,3*H*)-dithione] have been solvothermally synthesized. The luminescent complexes **1** and **2** provide remarkable structural diversity depending on different reaction solutions. Complex **1** consists of a discrete pseudo-hexagonal prismatic $[\text{Cu}_6\text{S}_6]$ core that can be described as two stacked, chair-shaped $[\text{Cu}_3\text{S}_3]$ rings bound together by the C–N bridges of the atdm ligands, in which the atdm ligand was generated *via in situ* amination of H_2atd in the presence of DMF solution. Whereas complex **2** is a 2D (4,4) net based on single node Cu^{I} ions crystallized in acetonitrile, in which H_2atd ligands exist in the thione form atdH_2 and the partially deprotonated form atdH . Complex **3** has a two-fold interpenetrated (10,3)-a topological network based on unprecedented cobalt-centered trigonal-bipyramidal $[\text{Co}_6(\text{atd})_6]$ building blocks, linked by Cl^- double-bridges and showing oriented effects of aniline side groups. IR spectra, elemental analyses and XRD analyses confirmed the phase-purities of the as-synthesized complexes. The photoluminescence properties of **1** and **2** in the solid state and the magnetic properties of **3** are investigated. A discussion of the crystal structures, as well as the coordination properties of the multifunctional sulfur-containing ligands upon different geometries of the central units, is also provided.

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Introduction

The design and synthesis of novel polynuclear complexes or cluster-based metal–organic frameworks have attracted intense interest owing to their structural and topological diversity as well as the realization of their potential for use in magnetism, catalysis, gas storage, ion exchange, molecular recognition and optical properties, *etc.*¹ The utilization of polynuclear metal clusters as building blocks creates more opportunities to construct highly connected frameworks due to their large surface areas meaning they can more readily accommodate the steric demands of diverse linkers.² Various preparation methods have been proposed to obtain such coordination architectures. However, establishing the precise principles of constructing desirable architectures is still one of the major challenges in

coordination chemistry. The design of these complexes is highly influenced by factors such as the coordination nature of the metal ion, the structural characteristics of the organic ligand, the metal–ligand ratio, the solvent quality and other possible influences, which provides a possible approach to the controlled assembly and crystal growth process, with systematically tunable interesting properties.³ One of the most fruitful choices consists of taking advantage of heterocyclic thiones, such as pyridinethione,⁴ pyrimidinethione⁵ and 1,3,5-triazine-2,4,6-trithiol^{5c,6} as potentially ambidentate or multifunctional ligands. Their exocyclic sulfur atoms and heterocyclic nitrogen atom donors make them useful in developing different fantastic polynuclear complexes, especially coordination polymers.

We have recently been investigating the assembly of structurally novel or functional coordination polymers, in which various polynuclear copper(i) halide cluster units have been successfully introduced to act as secondary building units (SBUs).⁷ As a comparative study, we devoted more attention to using multicomponent assemblies to design and prepare polynuclear metal clusters with halide- and sulfur-containing mixed ligands and obtained an luminescent *acs* topological framework featuring an undecanuclear Cu^{I} SBU.⁸ Indeed, the incorporation of an S-donor as a bridge between adjacent

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†Electronic supplementary information (ESI) available: Fig. S1–S5, PXRD pattern for **1–3** (Fig. S6–S8), ¹H NMR spectra of **1** and **2** (Fig. S9 and S10) and UV-Vis spectra of reaction medium in the formation of **1**. CCDC 919307–919309 for **1–3**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt50165e

transition metal sites is more likely to induce core aggregation and highly desirable for luminescent behavior owing to the orbital energies being well matched for S atoms, which may afford large delocalization of the spin electron density toward the bridging atom.⁹ Moreover, the chemistry of the Cu–S clusters is extremely important in life systems, and it has been confirmed that yeast and mammalian metalloproteins that contain a Cu–S cluster, function as antioxidants.¹⁰ Following the above considerations, we chose 6-anilino-1,3,5-triazine-2,4-dithiol (H_2atd) as the original ligand. In comparison with 1,3,5-triazine-2,4,6-trithiol,^{5c,6} H_2atd obviously could be divided into two parts: triazine-2,4-dithiol and aniline group. The former is expected to be bridging groups with potential multidentate possibilities from deprotonated thiol and more than one coordinated active heterocyclic nitrogen atoms, while the latter can offer additional aromatic interactions and hydrophobic interactions to modulate and influence the assembly of the building structure. Nevertheless, until now, research on metal– H_2atd systems has not been well explored. Only two crystal structures of Sn-complexes with H_2atd have been documented in 2008.¹¹

Herein, we report the solvothermal syntheses and structures of three new coordination complexes and the investigation of the *in situ* ligand reaction, geometric effects and the differentiation of metal atom in different solvothermal systems on the crystal structures of these compounds. We selected Cu and Co atoms as metal nodes for assembly with H_2atd , respectively, and obtained one discrete hexameric cluster $[Cu^I_6(atdm)_6]$ (**1**), one coordination polymer $[Cu^I(Hatd)(H_2atd)]$ (**2**) with 2D (4,4) net and one 3D mixed-valence hexacobalt cluster-based metal-organic framework $[H_3O][Co^{II}_4Co^{III}_2Cl_3(atd)_6] \cdot H_2O$ (**3**) with (10,3)-*a* topology. Interestingly, the *atdm* ligand in **1** was obtained through the *in situ* substitution of one mercapto group for dimethylamino in the presence of DMF under solvothermal conditions, which led to an interesting structure different to that of **2** that crystallized from acetonitrile. In general, *in situ* metal ligand reactions as a non-conventional and interesting method may provide stable complexes that exhibit intriguing structural diversity for potential applications.¹² Although the complicated courses in relatively low-boiling-solvents and relatively high temperature could hardly be investigated, ligand reaction should not be simply regarded as a lucky coincidence but as a valuable opportunity to understand the self-assembly and crystal growth process. The solid-state luminescence spectra of **1** and **2** display strong red emission bands at room temperature, characteristic of the Cu^I complexes with chalcogen ligand. **3** exhibits magnetic properties with four Co^{II} centers antiferromagnetically coupled.

Materials and physical measurements

The reagents and solvents employed were commercially available and used as received without further purification. The C, H and N microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. The FT-IR spectra were

recorded from KBr pellets in the range 4000–400 cm^{-1} on a Bio-Rad FTS-7 spectrometer. X-ray powder diffraction (XRD) intensities for **1–3** were measured at 293 K on a Rigaku D/max-III A diffractometer (Cu-K α , $\lambda = 1.54056 \text{ \AA}$). The crushed single-crystalline powder samples were prepared by crushing the crystals and scanning from 3–60° with a step of 0.1° s^{-1} . Calculated patterns of **1–3** were generated with PowderCell. The emission/excitation spectra of **1** and **2** were measured on an FluoroMax-4 VPF-100 fluorescence spectrophotometer (HORIBA Jobin Yvon). Magnetic susceptibility measurements were performed with a Quantum Design MPMS-XL7 SQUID. A polycrystalline sample of **3** was embedded in vaseline to prevent torquing. Data were corrected for the diamagnetic contribution calculated from Pascal constants. 1H NMR spectra (500 MHz, $(CD_3)_2SO$) of **1** and **2** were obtained on a Bruker Avance 500 spectrometer using the solvent signal as internal standard. All δ values are given in ppm. The UV-VIS spectra were recorded with a Shimadzu UV-2450 spectrophotometer.

Syntheses of complexes 1–3

Synthesis of $[Cu^I_6(atdm)_6]$ (**1**)

CuI (0.285 g, 1.5 mmol) was dissolved in DMF (8 ml) at ambient temperature, followed by the addition of 6-anilino-1,3,5-triazine-2,4-dithiol (H_2atd , 0.236 g, 1.0 mmol) in DMF (8 ml) with vigorous magnetic stirring in a 25 ml Parr Teflon-lined stainless steel vessel. The mixture was heated for 3 days at 150 °C and then cooled to room temperature at a rate of 10 K h^{-1} . After cooling to room temperature, red block-like crystals were obtained in the yield of 90% (based on H_2atd). Phase purity of the bulk materials was confirmed by comparison of its powder diffraction pattern with that calculated from the single crystal study. Elemental analysis for **1** $C_{66}H_{72}Cu_6N_{30}S_6$, Calcd: C, 42.64; H, 3.90; N, 22.60. Found: C, 42.68; H, 3.87; N, 22.66. IR data (KBr) (400–4000 cm^{-1}): 3353m, 2929w, 1601s, 1571s, 1532s, 1475s, 1457w, 1446w, 1407s, 1381s, 1317m, 1230s, 1204s, 1083w, 1060w, 1030w, 999m, 958m, 896w, 865w, 822w, 791m, 753m, 718w, 689m, 664w, 623w, 607w, 572w, 499w.

Synthesis of $[Cu^I(Hatd)(H_2atd)]$ (**2**)

CuI (0.285 g, 1.5 mmol) was dissolved in acetonitrile (8 ml) at ambient temperature, followed by the addition of H_2atd (0.236 g, 1.0 mmol) in acetonitrile (8 ml) with vigorous magnetic stirring in a 25 ml Parr Teflon-lined stainless steel vessel. The mixture was heated for 6 days at 150 °C and then cooled to room temperature at a rate of 10 K h^{-1} . After cooling to room temperature, red block-like crystals were obtained in the yield of 75% (based on H_2atd). Phase purity of the bulk materials was confirmed by comparison of its powder diffraction pattern with that calculated from the single crystal study. Elemental analysis for **2** $C_{18}H_{15}CuN_8S_4$, Calcd: C, 40.40; H, 2.83; N, 20.94. Found: C, 40.47; H, 2.85; N, 21.02. IR data (KBr) (400–4000 cm^{-1}): 3446w, 3349m, 3291w, 3253w, 1635w, 1606m, 1575s, 1517s, 1487s, 1469w, 1450m, 1347m, 1292w,

Table 1 Crystallographic data for 1–3

	1	2	3
Empirical formula	C ₆₆ H ₇₂ Cu ₆ N ₃₀ S ₆	C ₁₈ H ₁₅ CuN ₈ S ₄	C ₅₄ H ₄₁ Cl ₃ Co ₆ N ₂₄ S ₁₂ O ₂ ^c
<i>M_r</i> /g mol ^{−1}	1859.14	535.16	1902.81
<i>T</i> /K	293	293	293
Crystal system	Triclinic	Monoclinic	Cubic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>Ia</i> $\bar{3}d$
<i>a</i> /Å	13.1431(8)	11.1491(6)	31.8956(6)
<i>b</i> /Å	13.4151(10)	10.3660(4)	31.8956(6)
<i>c</i> /Å	13.7079(9)	17.8580(9)	31.8956(6)
α /°	62.032(2)	90	90
β /°	64.169(1)	98.330(2)	90
γ /°	83.174(2)	90	90
<i>V</i> /Å ³	1910.2(2)	2042.10(17)	32 448.3(11)
<i>Z</i>	1	4	16
ρ_c /g cm ^{−3}	1.616	1.741	1.528
μ /mm ^{−1}	1.867	1.505	1.656
<i>F</i> (000)	948	1088	14 928
Reflns collected	14 062	7115	18 593
Unique reflns	7379	1984	2652
<i>R</i> _{int}	0.0312	0.0265	0.0575
<i>S</i>	1.074	1.087	1.140
<i>R</i> ₁ ^a (<i>I</i> > 2σ(<i>I</i>))	0.0354	0.0342	0.0528 ^d
w <i>R</i> ₂ ^b (All data)	0.1009	0.0812	0.1724 ^d

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$. ^c Including solvate molecules. ^d SQUEEZE.

1258m, 1211m, 1130s, 1125s, 958w, 876m, 822m, 765w, 753m, 728w, 704m, 684m, 661m, 619w, 503w, 460m.

Synthesis of [H₃O][Co^{II}₄Co^{III}₂Cl₃(atd)₆]·H₂O (3)

CoCl₂·6H₂O (0.238 g, 1 mmol) was dissolved in acetonitrile (8 ml) at ambient temperature, followed by the addition of H₂atd (0.118 g, 0.5 mmol) in acetonitrile (8 ml) with vigorous magnetic stirring in a 25 ml Parr Teflon-lined stainless steel vessel. The mixture was heated for 3 days at 160 °C and then cooled to room temperature at a rate of 10 K h^{−1}. After cooling to room temperature, deep purple crystals were obtained in the yield of 92% (based on H₂atd). Phase purity of the bulk materials was confirmed by comparison of its powder diffraction pattern with that calculated from the single crystal study. Elemental analysis for 3 C₅₄H₄₁Cl₃Co₆N₂₄S₁₂O₂, Calcd: C, 34.09; H, 2.17; N, 17.67. Found: C, 34.14; H, 2.21; N, 17.62. IR data (KBr) (400–4000 cm^{−1}): 3446m, 3289w, 1684w, 1605m, 1565m, 1514s, 1472s, 1452w, 1384s, 1326w, 1274m, 1228w, 1186m, 1047w, 988w, 886w, 830w, 772w, 755w, 725w, 689w, 623w, 503w.

X-ray crystallography

Single crystals of 1–3 suitable for X-ray analysis were obtained directly from the above solvothermal syntheses. The diffraction data of 1–3 was collected on a Bruker Smart Apex CCD diffractometer with graphite monochromated MoK α radiation (λ = 0.71073 Å) at 293 K. The data integration and reduction were processed with SAINT^{13a} software, and empirical absorption corrections were applied to the collected reflections with SADABS.^{13b} The structures were solved by direct methods and refined by the full-matrix least-squares method on *F*² with SHELXTL program package.^{14a} All non-hydrogen atoms were

refined with anisotropic displacement parameters. For 3, protons for lattice solvent water and the disordered guest water molecules could not be modeled properly, thus the program SQUEEZE,^{14b} a part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. 316 electrons per unit cell were recovered in one void; that is 19.75 electrons per formula unit. Lattice solvent water molecules (10 electrons per H₂O) were present, and the electrons recovered by SQUEEZE have been assigned as 2 water molecules per formula unit. The final chemical formula was estimated from the SQUEEZE results combined with the elemental analysis and TGA results (Fig. S4†). The TG curve of 3 showed that the first weight loss of 1.90% (calcd 1.89%) occurs below 97 °C and corresponds to the loss of 2 lattice water per formula in the as-synthesized sample. The phenyl ring of atd ligand was disordered at two positions with 50 : 50% refined occupancies. The details of crystallographic data and selected bond lengths and bond angles are provided in Tables 1 and 2.

Results and discussion

Structure of [Cu^I₆(atdm)₆] (1)

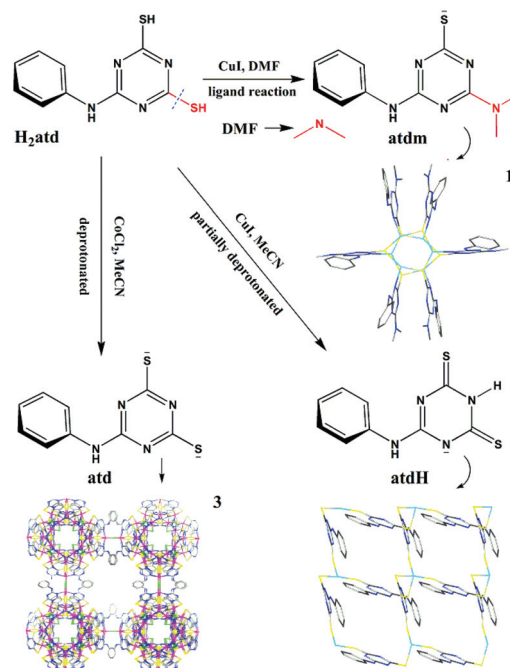
X-ray structural analysis of compound 1 shows that the compound crystallizes as discrete hexameric clusters and the asymmetric unit contains one half of the formula unit and consists of three crystallographically unique Cu^I atoms and three atdm ligands. The atdm ligand was synthesized *in situ* from H₂atd by replacement of one of mercapto groups of H₂atd with dimethylamino, which was derived from the cleavage of DMF at high temperature (Scheme 1). The N–C bond distances of the dimethylamine groups fall in the range 1.447–1.465 Å,

Table 2 Selected bond lengths (Å) and angles (°) for **1–3**^a

1			
Cu(1)–N(1)	2.040(2)	Cu(3)–S(2a)	2.2753(7)
Cu(1)–S(3a)	2.2658(7)	Cu(3)–S(1)	2.2275(7)
Cu(1)–S(2)	2.2632(7)	Cu(1)···Cu(3)	2.6802(5)
Cu(2)–N(6)	2.035(2)	Cu(1)···Cu(2)	2.7097(4)
Cu(2)–S(3)	2.2874(7)	Cu(2)···Cu(3)	2.7730(5)
Cu(2)–S(1)	2.2353(8)	Cu(2)···Cu(3a)	2.9338(5)
Cu(3)–N(11a)	2.048(2)		
N(1)–Cu(1)–S(2)	120.93(6)	N(1)–Cu(1)–S(3a)	121.82(6)
S(2)–Cu(1)–S(3a)	108.97(3)	N(6)–Cu(2)–S(3)	104.29(6)
N(6)–Cu(2)–S(1)	121.64(6)	S(1)–Cu(2)–S(3)	122.11(3)
N(11a)–Cu(3)–S(1)	121.85(6)	(1)–Cu(3)–S(2a)	119.65(3)
N(11a)–Cu(3)–S(2a)	106.87(7)		
2			
Cu(1)–S(1)	2.2672(7)	Cu(1)–S(2b)	2.4489(8)
Cu(1)–S(1a)	2.2672(7)	Cu(1)–S(2c)	2.4489(8)
S(1)–Cu(1)–S(1a)	126.55(5)	S(1)–Cu(1)–S(2c)	108.35(3)
S(1)–Cu(1)–S(2b)	105.53(3)	S(1a)–Cu(1)–S(2c)	105.52(3)
S(1a)–Cu(1)–S(2b)	108.35(3)	S(2b)–Cu(1)–S(2c)	99.27(4)
3			
Co(1)–N(1a)	2.106(4)	Co(2)–S(1c)	2.563(1)
Co(1)–N(1)	2.106(4)	Co(2)–S(1d)	2.563(1)
Co(1)–Cl(1a)	2.473(1)	Co(2)–S(1e)	2.563(1)
Co(1)–Cl(1)	2.473(1)	Co(3)–N(2c)	1.947(4)
Co(1)–S(1)	2.564(1)	Co(3)–N(2)	1.947(4)
Co(1)–S(1a)	2.564(1)	Co(3)–N(2e)	1.947(4)
Co(2)–S(1a)	2.563(1)	Co(3)–S(2)	2.281(1)
Co(2)–S(1b)	2.563(1)	Co(3)–S(2e)	2.281(1)
Co(2)–S(1)	2.563(1)	Co(3)–S(2c)	2.281(1)
N(1a)–Co(1)–N(1)	154.1(2)	S(1)–Co(2)–S(1d)	176.78(5)
N(1a)–Co(1)–Cl(1a)	93.9(1)	S(1c)–Co(2)–S(1d)	79.61(5)
N(1)–Co(1)–Cl(1a)	105.4(1)	S(1a)–Co(2)–S(1e)	79.61(5)
N(1a)–Co(1)–Cl(1)	105.4(1)	S(1b)–Co(2)–S(1e)	176.78(5)
N(1)–Co(1)–Cl(1)	93.9(1)	S(1)–Co(2)–S(1e)	97.98(3)
Cl(1a)–Co(1)–Cl(1)	83.67(7)	S(1c)–Co(2)–S(1e)	97.98(3)
N(1a)–Co(1)–S(1)	93.5(1)	S(1d)–Co(2)–S(1e)	84.51(5)
N(1)–Co(1)–S(1)	66.8(1)	N(2c)–Co(3)–N(2)	97.5(1)
Cl(1a)–Co(1)–S(1)	172.23(2)	N(2c)–Co(3)–N(2e)	97.5(1)
Cl(1)–Co(1)–S(1)	96.45(4)	N(2)–Co(3)–N(2e)	97.5(1)
N(1a)–Co(1)–S(1a)	66.8(1)	N(2c)–Co(3)–S(2)	166.5(1)
N(1)–Co(1)–S(1a)	93.5(1)	N(2)–Co(3)–S(2)	71.9(1)
Cl(1a)–Co(1)–S(1a)	96.45(4)	N(2e)–Co(3)–S(2)	92.3(1)
Cl(1)–Co(1)–S(1a)	172.23(2)	N(2c)–Co(3)–S(2e)	92.3(1)
S(1)–Co(1)–S(1a)	84.48(6)	N(2)–Co(3)–S(2e)	166.5(1)
S(1a)–Co(2)–S(1b)	97.98(3)	N(2e)–Co(3)–S(2e)	71.9(1)
S(1a)–Co(2)–S(1)	84.51(5)	S(2)–Co(3)–S(2e)	99.49(5)
S(1b)–Co(2)–S(1)	79.61(5)	N(2c)–Co(3)–S(2c)	71.9(1)
S(1a)–Co(2)–S(1c)	176.78(5)	N(2)–Co(3)–S(2c)	92.3(1)
S(1b)–Co(2)–S(1c)	84.51(5)	N(2e)–Co(3)–S(2c)	166.5(1)
S(1)–Co(2)–S(1c)	97.98(3)	S(2)–Co(3)–S(2c)	99.49(5)
S(1a)–Co(2)–S(1d)	97.98(3)	S(2e)–Co(3)–S(2c)	99.49(5)
S(1b)–Co(2)–S(1d)	97.98(3)		

^a Symmetry codes: (a) $-x+1, -y+2, -z+1$ for **1**; (a) $-x, y, -z+\frac{3}{2}$; (b) $x+\frac{1}{2}, y+\frac{1}{2}, z$; (c) $-x-\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$ for **2**; (a) $y-\frac{1}{4}, x+\frac{1}{4}, -z+\frac{1}{4}$; (b) $-x+\frac{3}{4}, -z+\frac{3}{4}, -y+\frac{3}{4}$; (c) $-y+1, z+\frac{1}{2}, -x+\frac{1}{2}$; (d) $z+\frac{1}{4}, -y+\frac{5}{4}, x-\frac{1}{4}$; (e) $-z+\frac{1}{2}, -x+1, y-\frac{1}{2}$ for **3**.

characteristic of N–C single bonds. The ¹H NMR data of complex **1** in solution (Fig. S9†) confirm the *in situ* formation of the new ligand 4-dimethylamino-6-anilino-1,3,5-triazine-2-thiolate (atdm) in complex **1**. ¹H NMR data show the dimethylamino protons appearing as a sharp single peak at $\delta = 3.11$ ppm. The crystal structure of compound **1** has no counter ions, indicating the valence of Cu to be +1 and the atdm ligand is in thiolate form. The molecule of **1** features as a pseudohexagonal prismatic [Cu₆S₆] core, which can also be view as

**Scheme 1** Schematic representation of the *in situ* ligand reaction and the deprotonated forms of H₂atd.

two stacked, chair-shaped [Cu₃S₃] rings bound together by the C–N bridges of the atdm ligand, with a centre of symmetry (Fig. 1b). As shown in Fig. 1a, each Cu^I atom is coordinated by one nitrogen atom (Cu–N = 2.035(2)–2.048(2) Å) and two sulphur atoms (Cu–S = 2.228(1)–2.287(1) Å) from three different atdm ligands in a trigonal arrangement. Each atdm ligand works as a μ_3 -bridging ligand to link three different Cu^I atoms (the thiolate-S atom is in μ_2 -bridging mode to connect two Cu^I atoms and the triazine-N atom connects to one Cu^I atom), defining a face of an octahedron and shortening the distances between Cu^I atoms. The Cu···Cu separations in the hexameric cluster range from 2.710–3.228 Å and each copper has two long and one short bonds to neighbouring copper atoms, where the longer Cu···Cu distances are between Cu atoms bridged through sulphur, while shorter distances are between Cu atoms bonded through the C–N bridges at the end of atdm ligands, which is slightly smaller than the sum of the van der Waals radii of two Cu^I atoms (2.8 Å). The Cu···Cu distances illuminate the possible existence of Cu···Cu interactions and the hexameric cluster lacks octahedral symmetry. These significant differences in the Cu···Cu distances are likely to be influenced by the minimal steric interaction between the peripheral atdm ligands and the orthogonal orientation of the ligands with respect to the copper octahedral face is able to contribute to the overall stability of the hexameric cluster. The six triazinyl rings and their substituent groups on the ligands lie alternately to each side of the 6-membered [Cu₃S₃] rings and spread outside the cluster to give a variant Ferris wheel appearance. There are four triazinyl rings of the atdm ligands belonging to two stacking pairs which stack to overlap each other in a face-to-face fashion. The center-to-center distance of

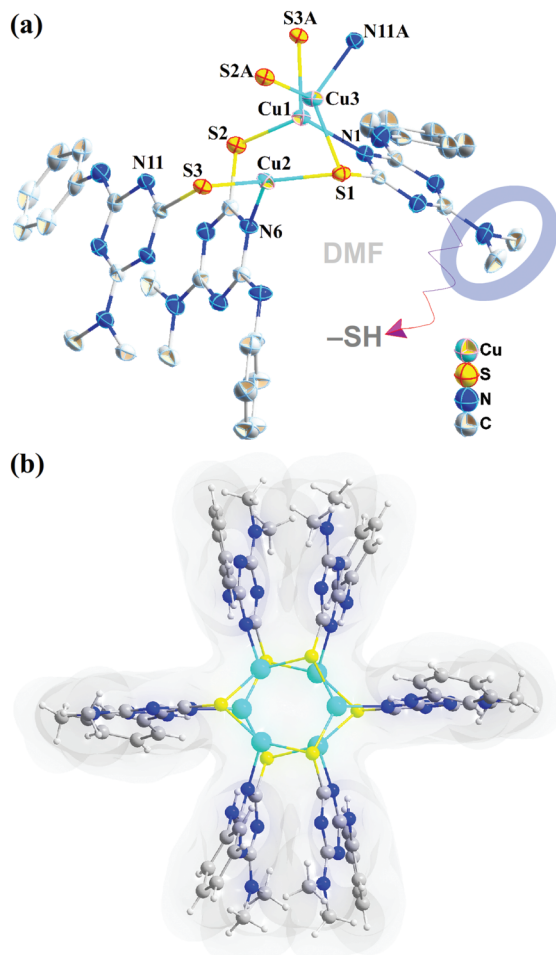


Fig. 1 (a) Ellipsoids views (50%) of the coordination geometries of Cu^{I} atoms in **1**. Some equivalent atoms have been generated to complete the Cu^{I} coordination, H atoms are omitted for clarity. Symmetry codes: (A) $-x + 1, -y + 2, -z + 1$. (b) Perspective view of the $\text{Cu}_6(\text{atdm})_6$ molecular with $\{\text{Cu}_6\text{S}_6\}$ cluster in **1**.

triazinyl rings is 3.28 \AA with the dihedral angle being 7.4° , which indicates significant $\pi \cdots \pi$ interaction. The hexameric clusters stack parallel to one another in a close-packed manner, so that each cluster has six nearest neighbors without obvious inter-cluster interactions (Fig. S1†). The cluster is close to those of a reported $[\text{Cu}_6\text{S}_6]$ core.¹⁵

It is reasonable to speculate that the presence of dimethylamine in the ligand derived from DMF solution reaction system unexpectedly may play a vital role in facilitating the formation of the hexameric clusters since a square-grids polymer of **2** is accessible by reaction of cuprous salt with H_2atd in acetonitrile. In the case of **2**, acetonitrile solvent does not show intense interference with the H_2atd ligand.

Structure of $[\text{Cu}^{\text{I}}(\text{Hatd})(\text{H}_2\text{atd})]$ (**2**)

The structure of **2** is a neutral 2D coordination network with the formula $[\text{Cu}^{\text{I}}(\text{Hatd})(\text{H}_2\text{atd})]$. The asymmetric unit contains one half of the formula unit and consists of one half Cu^{I} atom, one atdH or atd H_2 ligand with 50 : 50% occupancies. In detail,

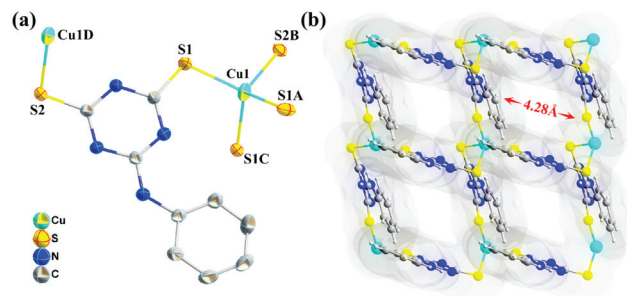


Fig. 2 (a) The coordination environment of Cu^{I} atoms in **2**. Some equivalent atoms have been generated to complete the Cu^{I} coordination, H atoms are omitted for clarity. (b) A 2D (4,4) layer in **2**.

the atd H_2 and atdH ligand are generated *via* proton transfer and/or partially deprotonated from H_2atd to compensate for the charge. The six C–N distances of the triazinyl rings of atdH ligand are slightly different ($1.331(3)$ – $1.384(3) \text{ \AA}$). The protons on the triazinyl-N atoms are unambiguously located from the difference map and can be distinguished by considering their hydrogen-bonding environment. The ^1H NMR data of complex **2** in solution are provided in the ESI (Fig. S10†), which justify the formation of the new ligand *via* proton transfer. ^1H NMR data show the triazinyl ring protons appearing as a single peak at $\delta = 13.09 \text{ ppm}$ and the $-\text{SH}$ proton to be absent, indicating transfer of the $-\text{SH}$ proton and the formation of Cu–S bonds. Cu^{I} shows a tetrahedral geometry and is ligated by four sulphur atoms from four different ligands with Cu–S distances of $2.267(1)$ – $2.449(1) \text{ \AA}$ (Fig. 2a). Each ligand is bound to two Cu^{I} atoms by using two sulphur atoms and the triazinyl-N atoms is protonated too, which prevents coordination, resulting in the formation of a 2D network based on (4,4) topology (Fig. 2b). The 2D grid lies in the *ab* crystallographic plane and contains rhombus openings of a minimum size $4.28 \times 4.28 \text{ \AA}$ as defined by the shortest transannular distance factoring van der Waals radii. The layers are noninterpenetrated despite the large cavity size. The adjacent grids are stacked offset with respect to each other in an ABAB fashion. Interestingly, the phenyl rings of the ligands pointed outside the layers insert deeply into the cavity of the adjacent layers and hence maximize the intermolecular interactions for a complementary shape (Fig. S2†). The distance between the mean planes of phenyl rings of 3.78 \AA suggests that $\pi \cdots \pi$ interactions are not accepted. Thus, mutual repulsion and steric hindrance of the aniline side groups play a vital role in the construction of the packing structure. Weak interlayer nonclassical N–H \cdots S and N–H \cdots N hydrogen bondings (N \cdots S = 3.297 – 3.350 \AA , N \cdots N = 3.457 \AA) have been observed.

Structure of $[\text{H}_3\text{O}][\text{Co}^{\text{II}}_4\text{Co}^{\text{III}}_2\text{Cl}_3(\text{atd})_6] \cdot \text{H}_2\text{O}$ (**3**)

The structure of compound **3** is highly influenced by the factor of the coordination nature of the metal ion and the side groups effect of the ligand. A mixed-valence hexacobalt cluster-based three-dimensional (3D) *srs* network of **3** has been solvothermally synthesized by the reaction of cobalt chloride and

H₂atd in acetonitrile. X-ray structural analysis shows that **3** crystallizes in the cubic space group *Ia* $\bar{3}$ *d*. The asymmetric unit contains one sixth of the formula unit and consists of three crystallographically Co atoms, one Cl[−] atom and one 6-anilino-1,3,5-triazine-2,4-bisthiolate ligand (atd). All atoms of the atd ligand localize in general positions. The Co1^{II} and Cl1 reside on the same symmetry site with 1/2 probability, while the Co2^{II} and Co3^{III} localize at the symmetry sites with the occupancies of 1/6 and 1/3, respectively. In detail, Co1^{II} is octahedrally coordinated by two μ_2 -Cl atoms (Co–Cl = 2.474(2) Å), two thiolate-S atoms (Co–S = 2.564(1) Å) and two triazinyl-N atoms (Co–N = 2.106(4) Å) from two different atd ligands, whereas Co2^{II} shows an octahedral sphere composed of six thiolate-S atoms (Co–S = 2.563(2) Å) from six different atd ligands. Co3^{III} is surrounded by three thiolate-S atoms (Co–S = 2.281(2) Å) and three triazinyl-N atoms (Co–N = 1.947(4) Å) from three different atd ligands (Fig. 3a). One solvated proton H₃O⁺ per formula balancing the framework charge and one guest water molecule are disordered.

Every six atd ligands are arranged in three groups of parallel pairs around six Co atoms and enlase the Co atoms in the

tridentate bridging modes, which leads to a hexanuclear cobalt cluster with *D*_{3h} symmetry (Fig. 3b). The highly symmetric cluster involves three equatorial Co1 atoms and two apical Co3 atoms arranged at the apexes of a trigonal bipyramid (Co1...Co3 = 5.785 Å), while Co2 atom is found to be located in the center of the *closo* cage (Co2...Co1 = 3.797 Å and Co2...Co3 = 4.365 Å, respectively) with the three equal Co1*–Co2–Co1** angles being 120° and the Co3–Co2–Co3* angle being 180°. The uncommon cobalt-centered trigonal-bipyramidal cluster unit is greatly different from the other known hexacobalt examples that are usually assembled as linear strings,¹⁶ cyclic units¹⁷ or octahedra.¹⁸

The hexanuclear cobalt cluster is three-connected to nearest neighbors *via* the Cl[−] double-bridging to the Co1 atoms that point outward from the cluster (Co1...Co1* = 3.684 Å), which results in a two-fold interpenetrated 3D coordination polymer (Fig. 3c). The shortest centroid...centroid distance of the adjacent hexanuclear cluster is *ca.* 11.28 Å. From the topological point of view, the 3D framework in **3** is a (10,3)-*a* net with the hexanuclear cluster as trigonal-planar node (also called the *srs* net; Fig. 3d). Such a net structure with the long Schläfli symbol

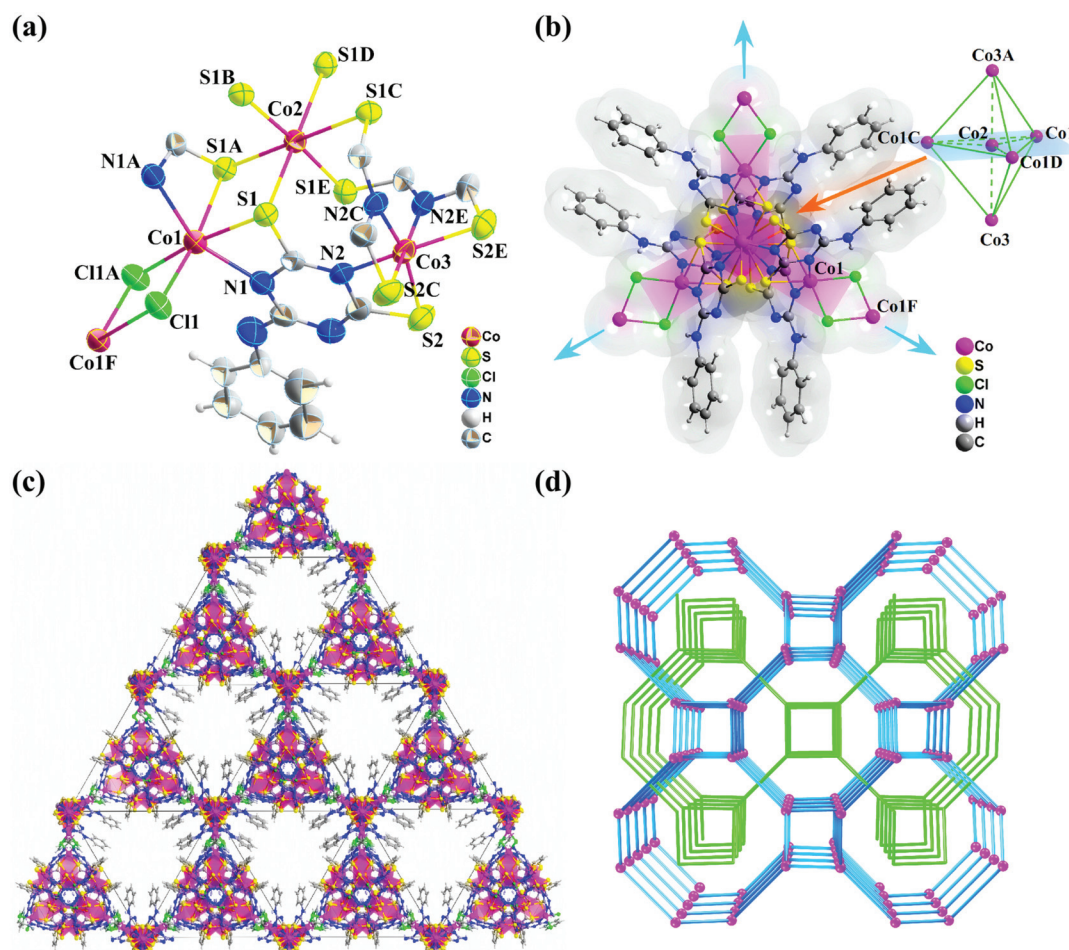


Fig. 3 (a) Ellipsoids views (50%) of the coordination geometries of Co atoms in **3**. Some equivalent atoms have been generated to complete the Co coordination. (b) The connectivity of the three-connected [Co₆] cluster. (c) One of the two-fold interpenetrating 3D frameworks in **3** with large channels in the single-net along the [111] direction. (d) The twofold interpenetrating (10,3)-*a* topological net based on the [Co₆] nodes along the *a*-axis.

of $10_5, 10_5, 10_5$ is one of seven (10,3) nets in which the shortest circuit including any 3-connecting node is 10-membered.¹⁹ The (10,3)-*a* topology is also one of the most frequently observed structure types in interpenetrating MOFs. However, to our knowledge, **3** is the first (10,3)-*a* net constructed by the hexanuclear cobalt cluster.

It is worth noting that there are two types of one-dimensional (1D) channels along the *a* (*b* or *c*) axis and [111] direction in the 3D single-net of **3**. The channels along the *a*, *b* and *c* axes are the same and feature a cross-shaped window (Fig. S3†), while the position of the phenyl rings of atd ligands cause the shape of the channel in the [111] direction to be hexagram-shaped. The pore dimensions along the *a* (*b* or *c*) axis and [111] direction are 6.02 and 9.44 Å, respectively, calculated by the spaces between the H atoms of phenyl rings of atd ligands (taking account of the van der Waals radii). Each single-net interpenetrates the other identical one, resulting in two-fold interpenetrated nets with baby-sized pores.

Photoluminescent properties of **1** and **2**

The photoluminescent properties of compounds **1** and **2** have been studied in the solid state. The excitation and emission maxima ($\lambda_{\text{max}}^{\text{ex}}$ and $\lambda_{\text{max}}^{\text{em}}$) of **1** and **2** at room temperature are depicted in Fig. 4. Upon excitation at 290 and 467 nm, **1** and **2** in the solid state exhibit strong photoluminescence at room temperature with emission maxima at *ca.* 636 and 594 nm, respectively. For the hexameric Cu^I cluster of **1** with sulfur-containing ligand in which partial Cu...Cu distances are shorter than the sum of the van der Waals radii, ligand-centered $\pi-\pi^*$ (LC) transition and metal to ligand charge transfer (MLCT) do not appear likely, considering the potential high adsorption

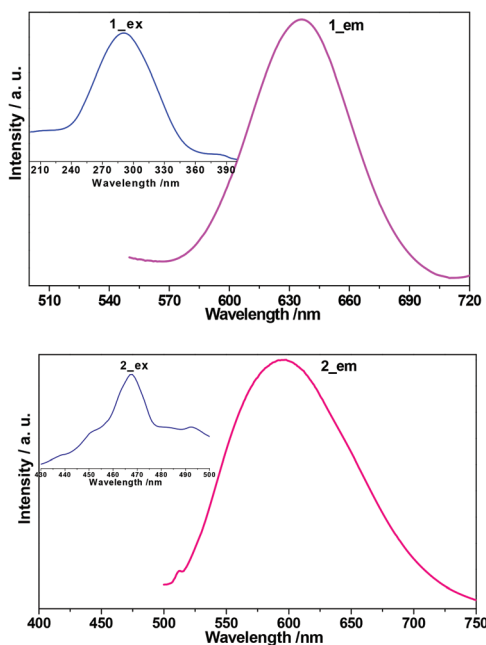


Fig. 4 Excitation (inset) and emission spectra of **1** (top) and **2** (bottom) in the solid state at room temperature.

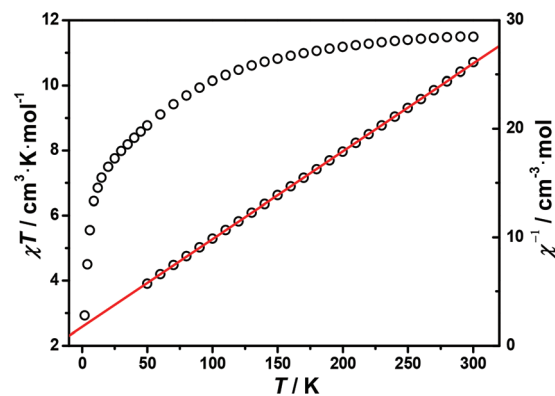


Fig. 5 Plots of χT versus T at an applied field of 500 Oe for **3**.

bands energy of the ligand atdm and the high π^* orbitals energy being unsuited for serving as an acceptor orbital for low-lying MLCT states, respectively. In comparison with the photoluminescent properties of other reported Cu^I-thiolate clusters, the emission of **1** is tentatively assigned as originating from the ligand to metal charge transfer (LMCT) characters, mixed with metal-centered (ds/dp) states modified by Cu...Cu interactions with the [Cu₆S₆] cluster.^{5b,20} For **2**, the emission of the Cu^I complex with chalcogen ligand in this region has been ascribed to be dominated by a LMCT (S→Cu) character.^{5c,20a}

Magnetic properties of **3**

A variable-temperature dc magnetic susceptibility measurement was performed on a microcrystalline powder sample of **3**, revealing a room-temperature χT value of 11.5 cm³ K mol⁻¹ (Fig. 5). This value is much larger than the spin-only ($S = 3/2$, $g = 2$) value of four high-spin Co^{II} ions (7.5 cm³ K mol⁻¹), due to the significant spin-orbit coupling of the octahedral Co^{II} ions.²¹ Upon cooling, the χT value product decreases gradually before 40 K, and then sharply decreases to a minimum value of 2.93 cm³ K mol⁻¹ at 2.0 K, due to the presence of antiferromagnetic exchanges between the Co^{II} ions and/or the orbital attribution of the distorted octahedral Co^{II} cations. Above 50 K, the magnetic susceptibilities follow Curie-Weiss behaviour with a Curie constant of 12.36(1) cm³ K mol⁻¹ and a Weiss constant of -21.5(2) K. The negative Weiss constant also indicates the presence of dominant antiferromagnetic interactions.

The isothermal field-dependent magnetization of complex **3** was measured at 1.8 K up to 7.0 T (Fig. S5†). The gradually-increasing variation of M versus H without saturation further confirms the antiferromagnetic coupling between the Co^{II} ions.

Discussion

Novel hydro/solvothermal *in situ* metal ligand reactions as a non-conventional method have provided a few novel functional coordination compounds, as well as unusual organic ligands that are inaccessible or not easily obtainable by conventional

methods.²² Some unexpected ligand reactions involved in the hydrolysis²³ or decarbonylation²⁴ of *N,N*-dimethylformamide (DMF) and the S–C(sp²) bond cleavage of organosulfides^{4d,7c} have been found. Compounds **1** and **2** were prepared by using CuI and H₂atd in the same molar ratio under solvothermal conditions in the DMF or MeCN. However, the final products are quite different. **1** is a discrete hexameric cluster compound with its *in situ* aminated ligand rather than a two-dimensional layer of **2**, which demonstrates that solvent reactivity is crucially important in the structure versatility. The possible reaction mechanism is the slow hydrolysis of DMF at high temperature giving rise to dimethylamino[•], which then reacts with the free-radical 6-anilino-1,3,5-triazine-2-thiol[•] intermediate resulted from cleavage of the S–C(sp²) bond of H₂atd to generate the atdm ligand (Scheme 1). The UV-Vis analysis of the mother liquid confirms the existence of formic acid as a by-product (Fig. S11†). It is interesting to ask why dimethylamine only replaces one of mercapto groups of H₂atd in the case of **1**. These may be due to the simultaneous competition and cooperation between coordination self-assembly and ligand reaction, and the tendency is that the core aggregation and the ligands themselves are able to not only protect the reserved S atoms but effectively stabilize them in the crystal form.

The coordination geometry of the central metal ion may have a very significant effect on the final structure. As demonstrated by the comparison of Co-complex **3** with Cu-complexes **1** and **2**, the change in coordination geometry of the trigonal or tetrahedral (Cu) to octahedral (Co) causes the distinctness of the linking fashion of the atd ligand and finally results in the formation of different cluster cores. It should also be noted that the other structure-influencing factors, such as auxiliary small ligand and side group effect, could affect the overall structure obtained.^{7d} In **3**, the introduction of strongly coordinating anion Cl[–] is a critical factor for the modification of topological connectivity and increasing the dimensionality of the network, which results in a (10,3)-*a* net. The control experiments carried out by using CoBr₂, Co(SO₄)₂ or Co(NO₃)₂ to replace CoCl₂ failed to obtain any single-crystal product under identical conditions, presumably because of the higher nucleophilicity of the Cl[–] anion in acetonitrile. It is interesting that all phenyl ring side groups of atd ligands point toward the center of the channels in the single-net of **3**, indicating that a hydrophobic surface is essential for the formation of the hexanuclear cobalt cluster-based framework. Compared with other assembly strategies, the side group directed approach has been proven to be very effective even when such side groups can only form very weak hydrophobic interactions.²⁵ A one-pot solvothermal approach involving a mixture of Co^{II} ions and organic ligand appears to be an unusual pathway to obtain mixed valence Co structures, where the molecular oxygen in air, high temperature and long time are responsible for *in situ* oxidation of the Co^{II} to Co^{III}. Otherwise, the type and coordination mode of the ligands is correlated to the metal oxidation state. However, only very limited examples of Co^{II} to Co^{III} oxidation have been found so far.²⁶

Conclusions

In summary, two copper and one cobalt complexes were synthesized with an *N*-heterocyclic thione ligand through solvothermal reactions. The thiol-copper complexes **1** and **2** possess discrete hexameric clusters and a 2D (4,4) net, respectively, producing red luminescence. Complex **3** is a two-fold interpenetrated (10,3)-*a* topological framework featuring an unprecedented cobalt-centered trigonal-bipyramidal cluster SBU. They show diverse structures and dimensionalities resulted from the unexpected ligand reaction or different coordination geometries of metal ions, which can be tuned by the reaction conditions. The results obtained here provide a hint for synthesizing new cluster-based structures of functional materials by using multifunctional sulfur-containing ligands with interesting side groups. The potential of this strategy to produce a cluster-based MOF using suitable sulfur-containing ligands is currently under way in our laboratory.

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