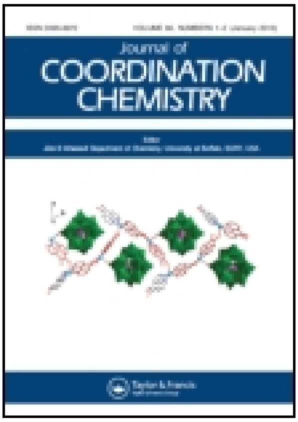

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Tetranuclear Zn(II) complexes with compartmental and dicyanamido ligands: synthesis, structure, and luminescent properties

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Tetranuclear Zn(II) complexes with compartmental and dicyanamido ligands: synthesis, structure, and luminescent properties

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New tetranuclear compounds have been obtained by reacting binuclear complexes, $[Zn_2L^n(\mu\text{-}OH)(H_2O)_2](ClO_4)_2$, with sodium dicyanamide (HL^n are end-off bicompartmental ligands resulting from condensation between 2,6-diformyl-*p*-cresol with *N*,*N*-dimethyl-ethylenediamine or 2-aminomethyl-pyridine). The complexes, $[\{L^1(\mu\text{-}OH)Zn_2\}(\mu_{1,5}\text{-}dca)_2\{Zn_2(\mu\text{-}OH)L^1\}](ClO_4)_2$ (**1**) and $[\{Zn_2L^2(\mu_3\text{-}OH)(dca)\}_2](ClO_4)_2 \cdot 2H_2O$ (**2**), have been characterized by single-crystal X-ray diffraction. The angular nature of the bridging dicyanamido induces the "M" shape of the tetranuclear cationic unit in **1**. The tetranuclear cation, because of its particular shape, acts as a receptor toward one perchlorate ion, which is hydrogen bonded to the hydroxo groups. This tetranuclear unit in **2** has a defective heterocubane structure. The luminescence properties of the new tetranuclear complexes have been investigated.

Keywords: Zinc complexes; Tetranuclear complexes; Molecular rectangle; Schiff-base ligands; Luminescence

1. Introduction

The self-assembly processes of molecular species into well-defined crystalline architectures represents a fascinating area in modern coordination chemistry. By using various transition metal ions, with preference for a particular stereochemistry, and suitably designed ligands, various topologies, such as molecular grids [1], helicates [2], racks [3], ladders [4], squares [5], and rectangles [6], have been obtained.

Schiff bases are very popular ligands because they efficiently act as chelates generating a rich variety of coordination compounds, ranging from mononuclear to polynuclear species [7]. An important class of Schiff-base ligands is represented by

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molecules able to accommodate two metal ions, either identical or different (bicompartmental ligands) [7, 8]. Usually, this type of ligand provides square-planar surroundings for each metal ion. In order to saturate the coordination number of metal ions preferring, for example, square pyramidal and octahedral environments, various ligands such as N_3^-, NCS^-, NCO^-, carboxylates, solvent molecules can be attached. When divergent ligands are employed (e.g., bis-4-pyridyl derivatives, dicarboxylato ions) tetranuclear and polynuclear complexes are assembled [9]. Another bridging ligand of interest is the dicyanamido anion [$dca^- = N(CN)_2^-$] [10]. This ligand may induce a variety of topologies and interesting magnetic properties due to its versatile coordination modes (e.g., monodentate, bis-monodentate, tris-monodentate, etc.) [10].

Recently, we have systematically explored the ability of homobinuclear $[Zn_2L^n]^{2+}$ complex cations to function as building blocks in the construction of metallosupramolecular architectures [4b, 11]. The self-assembly processes between binuclear $[Zn_2L^n]^{2+}$ cations and neutral *exo*-bidentate ligands (e.g., 4,4′-bipyridine, bis(4-pyridyl)ethane) or anionic metallocomplexes containing potentially bridging ligands, $[M(CN)_2]^-$ [M(I) = Ag(I), Au(I)], generate 1-D coordination polymers with different topologies and interesting luminescence properties.

As an extension of our work, in this article we report on new tetranuclear complexes obtained using homobinuclear zinc(II) complexes and the dicyanamido anion.

2. Experimental

Syntheses of $[\{L^1(\mu\text{-OH})Zn_2\}(\mu_{1,5}\text{-dca})_2\{Zn_2(\mu\text{-OH})L^1\}](ClO_4)_2$ (**1**) and $[\{Zn_2L^2(\mu_3\text{-OH})(dca)\}_2](ClO_4)_2 \cdot 2H_2O$ (**2**): all starting materials were of reagent grade and used without purification. The binuclear precursors were synthesized *in situ* by reacting Schiff bases with zinc perchlorate in the presence of LiOH.

Caution! Perchlorate salts are potentially explosive and should be handled in small quantities.

Infrared (IR) spectra were recorded as KBr pellets on a JASCO FTIR 4100 spectrophotometer from 4000 to 400 cm^{-1}. Absorption spectra were made with a JASCO V-670 spectrophotometer using MgO as a standard. The photoluminescence measurements were carried out at room temperature using a JASCO FP 6500 spectrofluorometer.

2.1. *Synthesis*

2.1.1. Synthesis of $[\{L^1(\mu\text{-OH})Zn_2\}(\mu_{1,5}\text{-dca})_2\{Zn_2(\mu\text{-OH})L^1\}](ClO_4)_2$ (1). Two ethanolic solutions containing stoichiometric amounts of 2,6-diformyl-*p*-cresol (0.1 mmol, 10 mL) and *N*,*N*-dimethyl-ethylenediamine (0.2 mmol, 5 mL) were mixed and kept under continuous stirring for 30 min at 50°C. The resulting solution was then reacted with 0.1 mmol of LiOH (in 5 mL H_2O) and $Zn(ClO_4)_2 \cdot 6H_2O$ (0.2 mmol, 10 mL ethanol) and kept under stirring for another 30 min. An ethanolic solution (10 mL) containing the sodium dicyanamide (0.1 mmol) was added to the solution containing the dinuclear precursor $[L^1Zn_2(\mu\text{-OH})](ClO_4)_2$. Slow evaporation of the mixture at room temperature led, after several days, to yellow crystals. Yield *ca* 85%. Elemental chemical analysis: Calcd for $C_{38}H_{56}Cl_2N_{14}O_{12}Zn_4$ (%): C, 36.97; H, 4.54; N, 15.89. Found (%): C, 37.04; H, 4.90; N, 15.86. IR data (KBr, cm^{-1}): 3553(s), 2971(m), 2912(m), 2883(m), 2848(m), 2355(s), 2275(shoulder), 2221(vs), 1648(vs), 1625(s), 1545(s), 1461(m), 1410(m), 1373(m), 1340(m), 1278(w), 1236(m), 1102(vs), 1076(shoulder), 976(w), 945(w), 895(w), 825(m), 779(m), 662(m), 548(w).

2.1.2. Synthesis of $[\{Zn_2L^2(\mu_3\text{-}OH)(dca)\}_2](ClO_4)_2 \cdot 2H_2O$ (2). Compound **2** has been obtained following the same general procedure described for **1** using 2-aminomethylpyridine instead of *N*,*N*-dimethyl-ethylenediamine. Yield *ca* 65%. Elemental chemical analysis: Calcd for $C_{46}H_{44}Cl_2N_{14}O_{14}Zn_4$ (%): C, 40.90; H, 3.26; N, 14.52. Found (%): C, 41.90; H, 3.22; N, 14.49. IR data (KBr, cm^{-1}): 3437(m), 3075(w), 2911(w), 2304(m), 2232(m), 2178(vs), 1647(vs), 1608(s), 1554(s), 1489(m), 1448(m), 1417(s), 1335(m), 1291(w), 1127(vs), 1067(s), 924(w), 886(m), 827(m), 771(m), 629(s), 558(m).

2.2. *X-ray structure determination*

X-ray diffraction measurements were performed on a STOE IPDS II diffractometer for **1** and on an Xcalibur E diffractometer for **2**, both operating with Mo-Kα ($\lambda = 0.71073$ Å) X-ray tube with graphite monochromator. The structures were solved by direct methods and refined by full-matrix least-squares based on F^2. The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using SHELX-97 crystallographic software package. A summary of the crystallographic data and the structure refinements for **1** and **2** is given in table 1.

Table 1. Crystallographic data and details of the structure refinement parameters for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{38}H_{56}Cl_2N_{14}O_{12}Zn_4$	$C_{46}H_{44}Cl_2N_{14}O_{14}Zn_4$
Formula weight ($g\,mol^{-1}$)	1233.34	1349.33
Temperature (K)	293	200
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	*Pnam*	*C2/c*
Unit cell dimensions (Å, °)		
a	13.275(3)	16.9430(11)
b	11.687(2)	16.0018(13)
c	34.025(7)	20.1901(12)
α	90	90
β	90	106.724(6)
γ	90	90
Volume ($Å^3$), Z	5278.8(18), 4	5242.4(6), 4
Calculated density ($g\,cm^{-3}$)	1.552	1.710
Absorption coefficient (mm^{-1})	1.965	1.990
$F(000)$	2528	2736
Goodness-of-fit on F^2	1.037	1.030
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0767$, $wR_2 = 0.1879$	$R_1 = 0.0401$, $wR_2 = 0.0960$
R indices (all data)	$R_1 = 0.1140$, $wR_2 = 0.2062$	$R_1 = 0.0530$, $wR_2 = 0.1049$
Largest difference peak and hole ($e\,Å^{-3}$)	0.921 and −0.776	0.753 and −0.830

3. Results and discussion

3.1. *Crystal structure*

This work illustrates the ability of the binuclear zinc complexes to generate tetranuclear compounds employing dicyanamido anion, $[N(CN)_2]^-$, as a spacer or terminal ligand. This approach is based on the observation that weakly bonded ligands (e.g., perchlorate or solvent), which are coordinated into the apical positions, can be replaced by potentially bridging ligands, resulting in tetranuclear complexes or coordination polymers.

By employing a homobinuclear $[Zn_2L^1]$ complex as a starting material (HL^1 is the Schiff base derived from 2,6-diformyl-*p*-cresol and *N*,*N*-dimethyl-ethylenediamine) and dicyanamido anion (dca^-) as a linker, we envisaged formation of tetranuclear complexes with the metal ions located in the corners of a rectangle. The crystallographic investigation of **1**, $[\{L^1(\mu\text{-OH})Zn_2\}(\mu_{1,5}\text{-dca})_2\{Zn_2(\mu\text{-OH})L^1\}](ClO_4)_2$, reveals, indeed, the presence of the desired tetranuclear entities and uncoordinated perchlorate anions (figure 1). The zinc(II) ions are five coordinate, with a square-pyramidal stereochemistry, the basal plane being formed by two nitrogen atoms arising from the Schiff-base ligand, and two oxygen atoms (one from the phenoxo endogenous bridge and the other from the hydroxo bridge). The apical positions are occupied by nitrogen atoms from the dicyanamido spacers [Zn1–N5 = 2.019(6), Zn2–N7 = 2.033(6) Å]. The intramolecular distances between the zinc ions are: Zn1···Zn2 = 3.050, $Zn1\cdots Zn1^{\#1} = 7.388$, and $Zn2\cdots Zn2^{\#1} = 7.653$ Å ($^{\#1}$= *x*, *y*, 0.5 − *z* – figure 1a). The angular nature of the bridging dicyanamido anion induces the "M" shape of the tetranuclear cationic unit (figure 1b). Interestingly, the tetranuclear cation, because of its particular shape, acts as a receptor toward one perchlorate, which is hydrogen bonded to the hydroxo groups – the O2(hydroxo)···O3(perchlorate) distance is 3.00 Å. The other perchlorate anion is disordered on two crystallographic positions with site occupancy factors of 0.5 each. Selected bond distances are given in table 2. The tetranuclear cations establish π–π stacking interactions (3.48–3.53 Å) with neighboring tetranuclear units generating supramolecular chains running along the crystallographic *c*-axis (figure 2).

Using a different Schiff base, HL^2, in the reaction with zinc perchlorate in the presence of LiOH, followed by the addition of sodium dicyanamide, a tetranuclear compound $[\{Zn_2L^2(\mu_3\text{-OH})(dca)\}_2](ClO_4)_2\cdot 2H_2O$ (**2**) has been assembled. Here the two dca^- ions act as monodentate terminal ligands. The tetranuclear $[Zn_4]^{2+}$ units are built up by binuclear moieties connected by two hydroxo groups which coordinate into the axial position of a zinc atom from the neighboring binuclear moiety (figure 3). This tetranuclear unit has a defective heterocubane structure and it was also observed in our

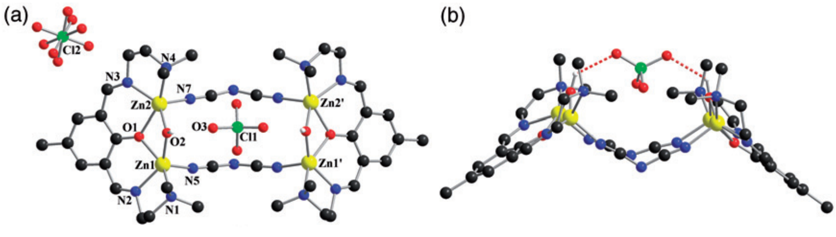

Figure 1. Orthogonal views of the tetranuclear complex in **1**, along with the atom labeling scheme.

previously reported 1-D systems: $^{1}_{\infty}[\{L^2Zn_2(\mu_3\text{-}OH)\}_2(H_2O)\{\mu\text{-}[Ag(CN)_2]\}](ClO_4)_3 \cdot THF \cdot 0.5MeOH$, $^{1}_{\infty}[\{L^2Zn_2(\mu_3\text{-}OH)\}_2(H_2O)\{\mu\text{-}[Au(CN)_2]\}](ClO_4)_3 \cdot THF \cdot H_2O$, containing the same bicompartmental ligand, HL^2 [11].

The four zinc ions are five-coordinate with a square-pyramidal stereochemistry. The basal planes for the five-coordinate zinc ions are formed by two nitrogen atoms and one phenoxo oxygen from the Schiff base, and one hydroxo oxygen atom (μ_3-OH). The apical positions of Zn1 and Zn1$^{\#1}$ ions ($^{\#1}$=$1-x$, y, $0.5-z$ – figure 3) are occupied by a nitrogen atom from the dicyanamido ligands that function as a terminal ligand. The bond lengths are Zn1–N1 = 2.101(3), Zn1–N2 = 2.048(3), Zn1–N5 = 1.984(4), Zn1–O1 = 2.060(3), and Zn1–O2 = 2.065(3) Å. For Zn2 and Zn2$^{\#1}$, the apical positions are occupied by hydroxo oxygen atoms from the neighboring binuclear moiety. The bond lengths around zinc ion are Zn2–N3 = 2.041(3), Zn2–N4 = 2.076(3), Zn2–O1 = 2.022(2), Zn2–O2 = 2.107(2), and Zn2–O2$^{\#1}$ = 2.005(3) Å ($^{\#1}$=$1-x$, y, $0.5-z$). Intramolecular π–π stacking interactions (3.38–3.68 Å) and intermolecular π–π stacking interactions (3.32–3.37 Å) are established between aromatic moieties of the the ligands, generating

Table 2. Selected bond lengths (Å) for **1** and **2**.

1	**2**
Zn1–N1 = 2.222(6)	Zn1–N1 = 2.101(3)
Zn1–N2 = 2.053(6)	Zn1–N2 = 2.048(3)
Zn1–N5 = 2.019(6)	Zn1–N5 = 1.984(4)
Zn1–O1 = 2.104(5)	Zn1–O1 = 2.060(3)
Zn1–O2 = 1.958(5)	Zn1–O2 = 2.065(3)
Zn2–N3 = 2.040(6)	Zn2–N3 = 2.041(3)
Zn2–N4 = 2.219(6)	Zn2–N4 = 2.076(3)
Zn2–N7 = 2.033(6)	Zn2–O1 = 2.022(2)
Zn2–O1 = 2.137(4)	Zn2–O2 = 2.107(2)
Zn2–O2 = 1.934(4)	Zn2–O2$^{\#1}$ = 2.005(3)

Symmetry code: $^{\#1} = 1-x$, y, $0.5-z$.

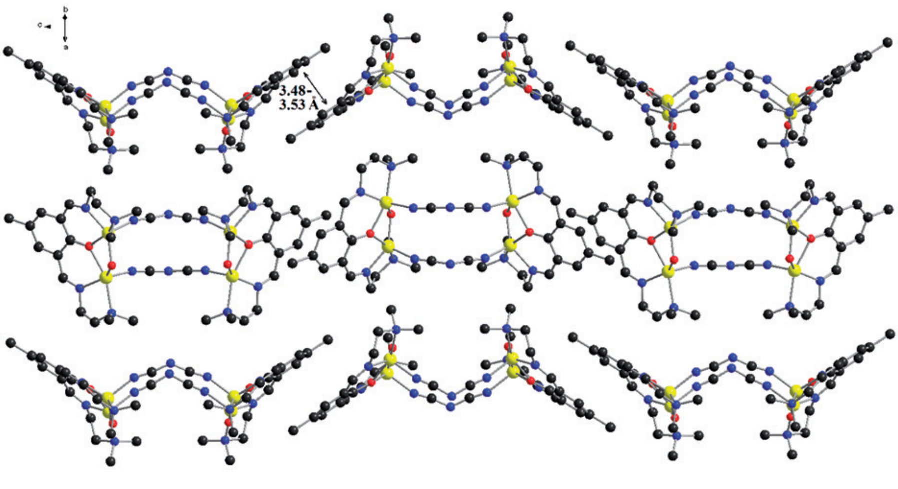

Figure 2. Packing diagram for crystal **1**, showing the π–π stacking interactions established between the Schiff bases from different tetranuclear units.

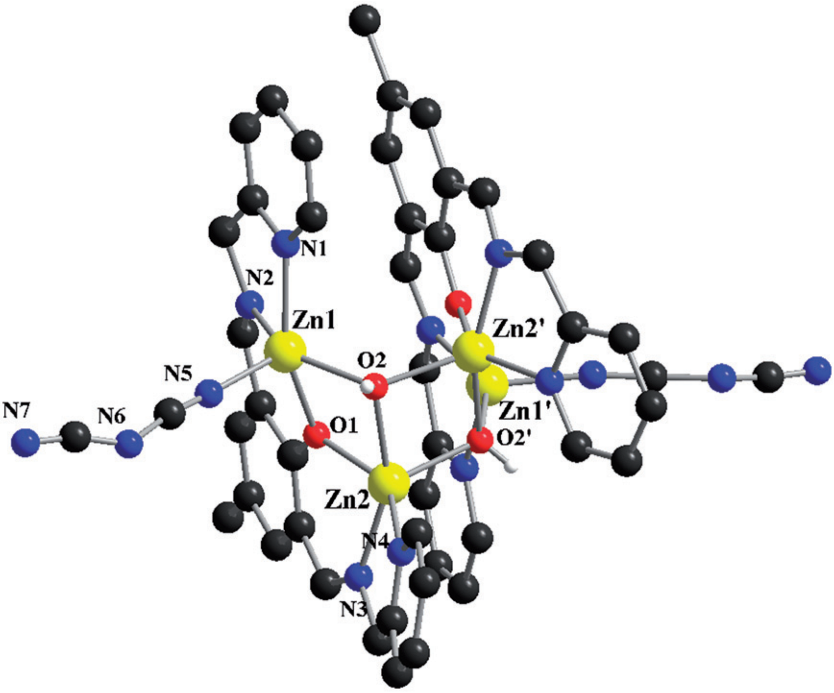

Figure 3. Perspective view of the tetranuclear complex in **2**, along with the atom numbering scheme.

supramolecular chains of tetranuclear cations. The intramolecular π–π contacts support the assembly of the tetranuclear unit by μ_3-OH bridges, favoring the formation of the defective heterocubane species over the rectangular one. A packing diagram of the tetranuclear complexes in crystal **2** is presented in figure 4.

The crystallization water molecules are involved in hydrogen bond interactions with uncoordinated cyano groups of the dicyanamido ligands ($N7\cdots O7W = 2.80$ Å).

3.2. *Spectral properties*

The IR spectra of compounds **1** and **2** show characteristic bands of the imine moieties from the Schiff-base ligands, of the dicyanamido ligand, and of the perchlorate anions. The bands of the dicyanamido ligand are due to the following vibrations modes: $\nu_s + \nu_{as}(N\equiv C)$, $\nu_s(N\equiv C)$ and $\nu_{as}(N\equiv C)$ [12]. The IR spectra of the two compounds are quite similar and exhibit three strong absorptions in the 2300–2170 cm^{-1} region, which are due to the dicyanamido ligand. The very strong band at 1648 cm^{-1} (**1**), 1647 cm^{-1} (**2**) is assigned to stretching of the iminic bond ($\nu_{C=N}$). Skeletal vibrations of the aromatic rings, representing C=C stretching, appear at 1545 cm^{-1} (**1**) and 1554 cm^{-1} (**2**). The perchlorate vibrations are observed as a very strong band at 1102 and 1076 cm^{-1} (**1**), 1127 and 1067 cm^{-1} (**2**), and a weak intensity band located at 662 cm^{-1} (**1**) and 629 cm^{-1} (**2**).

The electronic spectra of compounds **1** and **2** display bands with maxima at 385 nm, which are due to π–π* intraligand transitions.

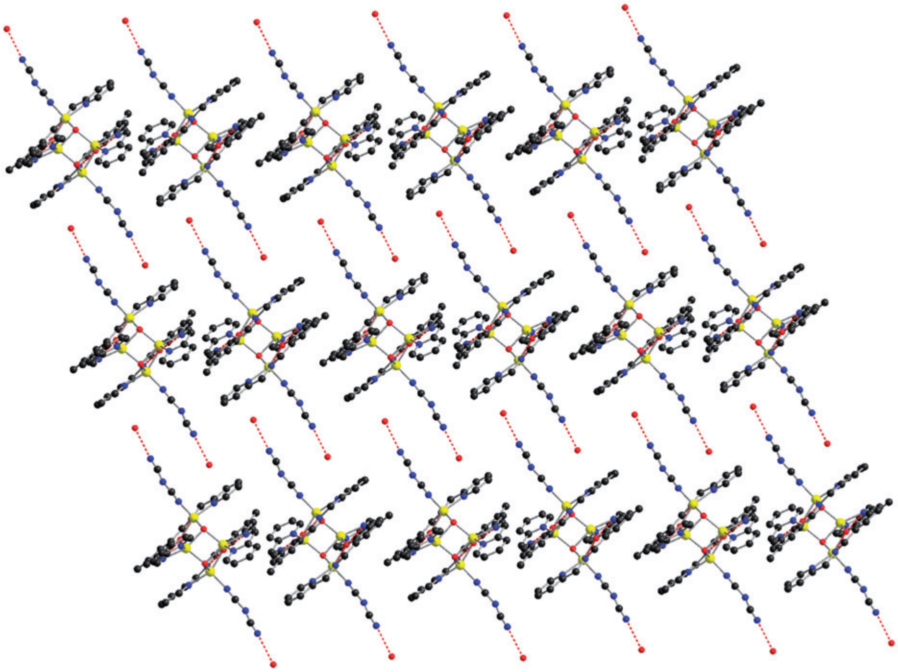

Figure 4. Packing diagram for crystal **2**, showing formation of the supramolecular chains and hydrogen bond interactions.

The luminescence properties of complexes which contain zinc(II) and Schiff bases or aromatic heterocyclic ligands are of interest because of their potential applications (e.g., chemical sensors, photochemistry, electroluminescent display, etc.) [13]. The coordination of the ligands to the metal ion increases the conformational rigidity of the ligand and reduces the loss of energy by radiationless thermal vibrations. The photoluminescent properties of **1** and **2** in the solid state at room temperature have been investigated. The emission as well the absorption spectra of **1** and **2** are depicted in figure 5. Both compounds exhibit luminescence with a peak maxima at $\lambda_{em} = 468$ nm for **1** and $\lambda_{em} = 491$ nm for **2**, when the excitation wavelength is varied between 350 and 400 nm. These bands are attributed to the intraligand $^1(\pi^*-\pi)$ fluorescent emissions.

4. Conclusions

We have synthesized two new zinc(II) tetranuclear compounds based on Schiff-base bicompartmental ligands and dicyanamido anions. In the self-assembly processes involving homodinuclear precursors and dicyanamido anions, the presence of additional aromatic fragments in the structure of bicompartmental ligands induces the aggregation of tetranuclear complex species with μ_3-OH bridges. The intramolecular π–π contacts favor the defective heterocubane tetranuclear topology over the rectangular one. Flourescence measurements reveal that these complexes exhibit luminescence at 468 nm (**1**) and 491 nm (**2**) (λ_{exc} varied between 350 and 400 nm).

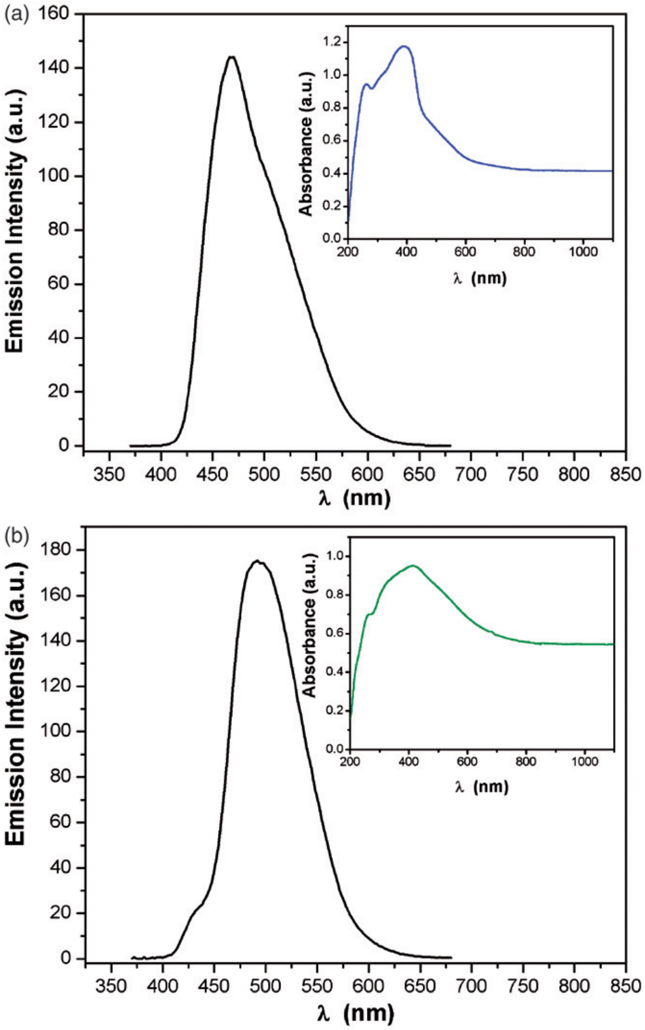

Figure 5. The emission spectra of **1** (a) and **2** (b) in solid state. The inset shows the UV-Vis spectra.

Supplementary material

CCDC reference numbers: 845744 (**1**), 845745 (**2**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

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