1,3,5-Triazapentanediene, A Novel Tridentate Ligand that Bridges Two Metal Ions in a κ^1*N*:κ^2*N* Bridging Mode with C_2 Symmetry

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The new mononuclear complexes [Ni(Htap)$_2$](ClO$_4$)$_2$ (**1**) and [Ni(tap)(Htap)]ClO$_4$ (**2**) were synthesized by the reaction of nickel(II) perchlorate and 1,3,5-triazine (Htap = 1,3,5-triazapentanediene). In **1** and **2**, neutral Htap and a monoanionic tap$^-$ coordinate in a square-planar mode to the nickel(II) ions (low-spin state) in a bidentate, chelating fashion. Using the central N of tap$^-$ of **2** as a donor atom, multinuclear complexes [{Cu(tren)}$_2${Ni(tap)$_2$}](ClO$_4$)$_4$ (**3**) and [Ni(Htap)$_2$]$_2$-[Ni{Ni(tap)(Htap)}$_2$(NCS)$_4$][Ni{Ni(tap)(Htap)}(NCS)$_5$]$_2$ (**4**) were synthesized. In both complexes, tap$^-$ binds two metal ions in a κ^1*N*:κ^2*N* bridging mode, with C_2 symmetry along the Ni–Cu axis for **3** and Ni–Ni axis for **4**.
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Introduction

Metal-containing ligands[1] are useful building blocks for making metal-assembled complexes with direct or indirect metal−metal interactions. In our recent studies, we have focused on a metal-containing ligand derived from 1,3,5-tris(2-pyridyl)-2,4,6-triazine (tptz). Upon refluxing, tptz can be converted into bis(2-pyridylcarbonyl)amine (Hpbca, Figure 1) or 2,4-bis(2-pyridyl)-1,3,5-triazapentanediene (Hbptap) in the presence of copper(II) ions; they were isolated as their copper(II) complexes (Scheme 1).[2−4,9] Hbpca was easily obtained as the free ligand,[2] and a variety of metal complexes were synthesized for use as metal-containing ligands.[2,5−8] We have shown that complexes such as [M(bpca)$_2$],[2,5−7] [Fe$_3$(μ$_3$-O)(bpca)$_4$(OEt)$_2$Cl$_4$]$^-$,[8] and [Cu(bptap)$_2$][9,10] potentially act as ligands to build metal-assembled complexes. In the resulting complexes, the two adjacent metal ions are bridged in a κ^1*N*:κ^2*O* mode for bpca$^-$ or κ^1*N*:κ^2*N* mode for bptap$^-$, with local C_2 symmetry along the metal−metal axis (Figure 2). When the two metal ions have dσ spins, this bridging mode causes the dσ orbitals to have different symmetry and thus makes them orthogonal to each other.[2,9,10] As a result, a ferromagnetic interaction occurs between the metal ions. While this coordination mode promotes ferromagnetic interactions, only a few reports have been published concerning either κ^1*N*:κ^2*O* or κ^1*N*:κ^2*N* modes.[11]

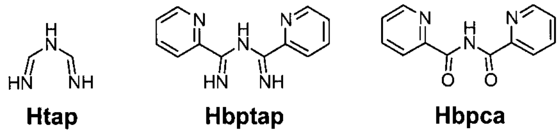
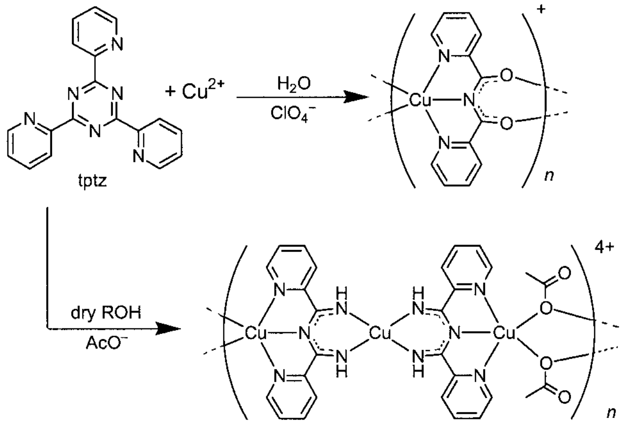


Figure 1. The structures of 1,3,5-triazapentanediene (Htap), 2,4-bis(2-pyridyl)-1,3,5-triazapentandiene (Hbptap), and bis(2-pyridylacarbonyl)amine (Hbpca)



Scheme 1

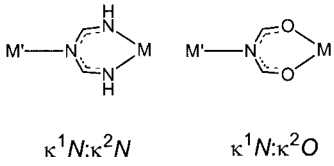


Figure 2. The κ^1*N*: κ^2*N* and κ^1*N*: κ^2*O* coordination mode with local C_2 symmetry found in complexes of bpca$^-$ and bptap$^-$

This study describes the simplest ligand in the series, 1,3,5-triazapentanediene (Htap, Figure 1), and its metal complexes. This ligand, like Hbptap, can link metals in a κ^1*N*:κ^2*N* mode. Unlike tptz, which requires severe con-

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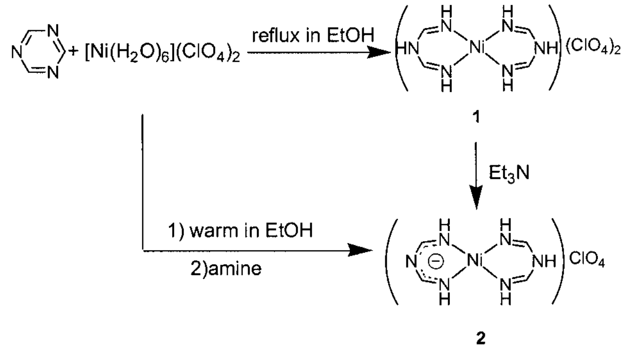
ditions to decompose, 1,3,5-triazine decomposes easily and Htap was first obtained as $[Cu(Htap)_2](ClO_4)_2$.[12] However, this copper(II) complex is not suitable as a metal-containing ligand since it decomposes under basic conditions. We found that 1,3,5-triazine is also converted into Htap in the presence of nickel(II) ions. Herein we report the syntheses of the new nickel(II) complexes $[Ni(Htap)_2](ClO_4)_2$ (**1**) and $[Ni(tap)(Htap)]ClO_4$ (**2**). The syntheses and structures of multinuclear complexes constructed with the complexed ligands, $[\{Cu(tren)\}_2\{Ni(tap)_2\}](ClO_4)_4$ (**3**) and $[Ni(Htap)_2]_2[Ni\{Ni(tap)(Htap)\}_2(NCS)_4][Ni\{Ni(tap)(Htap)\}(NCS)_5]_2$ (**4**), are also described.

Results and Discussion

Synthesis of Complexed Ligands 1 and 2

Unlike tptz, which forms stable metal complexes at room temperature, 1,3,5-triazine readily decomposes in the presence of metal ions to form Htap. At room temperature, the decomposition takes longer with nickel(II) than with copper(II), but upon heating to near reflux it was possible to prepare a new nickel(II) Htap complex, $[Ni(Htap)_2](ClO_4)_2$ (**1**) (Scheme 2).



Scheme 2

The mixed-ligand complex $[Ni(tap)(Htap)]ClO_4$ (**2**) was synthesized by controlling the basicity of the solution with ethylenediamine during the decomposition of 1,3,5-triazine. Slow diffusion of triethylamine into an alcoholic solution of **1** also gave the same product.

In order to obtain a pK_a value for **1**, ^1H NMR spectra of **1** and **2** in D_2O were measured. Both complexes have very broad signals at around $\delta = 9.38$ ppm for **1** and $\delta = 8.40$ ppm for **2**, which were not assigned. These broad peaks are indicative of a fast equilibrium between low-spin four-coordinate and high-spin six-coordinate geometries in aqueous solution, and therefore we could not determine a pK_a value for **1**.

Synthesis of Multinuclear Complexes 3 and 4

Complex **2** has a strong ability to act as a complexed ligand through the amide nitrogen atom of tap^-, and the trinuclear complex $[\{Cu(tren)\}_2\{Ni(tap)_2\}](ClO_4)_4$ (**3**) was easily synthesized by the reaction of **2** and $[Cu(tren)](ClO_4)_2$ in EtOH/H_2O. In this compound, a neutral $\{Ni(tap)_2\}$ moiety bridges two copper(II) ions to form a linear trinuclear complex acting as a bis-monodentate ligand (see below).

Addition of strong donor ions such as SCN^- to a solution of **2** resulted in the decomposition of **2** to give $\{Ni(NCS)_4\}^{2-}$ and $\{Ni(NCS)_5\}^{3-}$, and by controlling the reaction stoichiometry, a multinuclear complex $[Ni(Htap)_2]_2[Ni\{Ni(tap)(Htap)\}_2(NCS)_4][Ni\{Ni(tap)(Htap)\}(NCS)_5]_2$ (**4**) was obtained as crystals.

Structures of 1 and 2

The structures of complexes **1** and **2** are shown in Figures 3 and 4, respectively. In **1**, the nickel(II) ion is located on a crystallographic inversion center and the two Htap ligands in each molecule are equivalent. Both Htap ligands occupy four coordination sites of the square-planar nickel(II) ion in a bidentate chelating fashion with short Ni–N distances of 1.859(2) Å and 1.8554(18) Å, which results in the nickel(II) ion being in a low-spin state. The central nitrogen atom of the ligand (N2) is protonated, dividing the conjugated π-system, and, as a result, the terminal C–N bonds (C1–N1 and C2–N3) have a double bond character [C–N = 1.278(3) and 1.280(3) Å, respectively]. Each nitrogen atom in Htap is bound to oxygen atom(s) from ClO_4^- by hydrogen bonding(s) [O···N = 2.983(3)–3.136(2) Å].

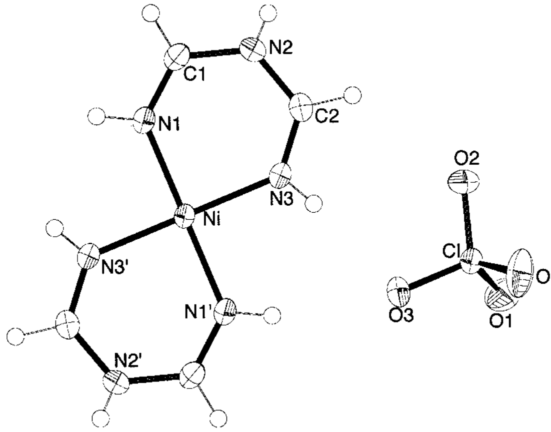


Figure 3. An ORTEP diagram of complex **1** with 50% displacement ellipsoids; relevant bond lengths (Å) and angles (°): Ni–N(1) 1.8554(18), Ni–N(3) 1.859(2), N(1)–C(1) 1.278 (3), C(1)–N(2) 1.348(3), N(2)–C(2) 1.356(3), C(2)–N(3) 1.280(3); N(3)–Ni–N(1) 90.08(9), N(1)–Ni–N(3′) 89.92(9); symmetry transformations used to generate equivalent atoms: ′ $-x, -y+1, -z$

In **2**, two crystallographically independent cations are present in the unit cell. They have similar structures and are abbreviated as complex **2a** [including Ni(1)] and complex **2b** [including Ni(2)]. $[Ni(tap)(Htap)]^+$ contains both a protonated Htap and a deprotonated tap^-. The structures of the Htap ligands in **2a** and **2b** are similar to that in **1**; however, tap^- shows slight differences from Htap, reflecting the differences in the electronic structures. The minus charge of tap^- is delocalized over the $N_{terminal}$–C–$N_{central}$–C–$N_{terminal}$ π-system, and, as a result, the double-bond character of the terminal C–N bonds is reduced and the

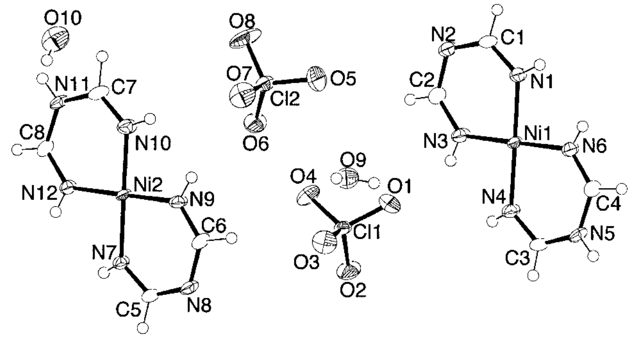


Figure 4. An ORTEP diagram of the complex $\mathbf{2}\cdot H_2O$ with 50% displacement ellipsoids

bond lengths are slightly elongated [for Htap the C−N$_{terminal}$ bond lengths are in the range between 1.276(4) and 1.285(4) Å; for tap$^-$ the distances are 1.306(4) and 1.297(4) Å for complex **2a** and 1.302(4) and 1.293(4) Å for complex **2b**); see also Table 1]. Both Htap and tap$^-$ coordinate to the nickel(II) ion, with slightly shorter Ni−N$_{terminal}$ bonds for tap$^-$ [1.837(3)−1.843(3) Å] than for Htap [1.860(3)−1.871(3) Å] due to the presence of the negative charge. Because of the strong ligand field, the nickel(II) ions are in a low-spin state. Each of **2a** and **2b** is aligned in a liner manner along the *a* axis and adjoining N$_{central}$(tap) and N$_{central}$(Htap) are connected by a hydrogen bonding [N(2)···N(5)* = 2.775(4) and N8···N(11)* = 2.791(4) Å].

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

Ni(1)−N(1)	1.837(3)	Ni(1)−N(3)	1.843(3)
Ni(1)−N(4)	1.863(3)	Ni(1)−N(6)	1.871(3)
N(1)−C(1)	1.306(4)	C(1)−N(2)	1.336(4)
N(2)−C(2)	1.338(4)	C(2)−N(3)	1.297(4)
N(4)−C(3)	1.280(4)	C(3)−N(5)	1.351(4)
N(5)−C(4)	1.362(4)	C(4)−N(6)	1.285(4)
Ni(2)−N(7)	1.845(3)	Ni(2)−N(9)	1.845(3)
Ni(2)−N(10)	1.860(3)	Ni(2)−N(12)	1.863(2)
N(7)−C(5)	1.302(4)	C(5)−N(8)	1.350(4)
N(8)−C(6)	1.339(4)	C(6)−N(9)	1.293(4)
N(10)−C(7)	1.282(4)	C(7)−N(11)	1.346(4)
N(11)−C(8)	1.360(4)	C(8)−N(12)	1.276(4)
N(1)−Ni(1)−N(3)	88.87(12)	N(1)−Ni(1)−N(4)	179.09(12)
N(3)−Ni(1)−N(4)	90.24(12)	N(1)−Ni(1)−N(6)	90.72(12)
N(3)−Ni(1)−N(6)	179.41(12)	N(4)−Ni(1)−N(6)	90.17(12)
C(1)−N(2)−C(2)	117.8(3)	C(3)−N(5)−C(4)	124.0(3)
N(9)−Ni(2)−N(7)	89.29(12)	N(9)−Ni(2)−N(10)	89.67(12)
N(7)−Ni(2)−N(10)	178.93(11)	N(9)−Ni(2)−N(12)	179.50(11)
N(7)−Ni(2)−N(12)	91.13(12)	N(10)−Ni(2)−N(12)	89.91(12)
C(6)−N(8)−C(5)	118.8(3)	C(7)−N(11)−C(8)	124.1(3)

Structure of Trinuclear complex 3

Figure 5 shows the crystal structure of trinuclear $[\{Cu(tren)\}_2\{Ni(tap)_2\}](ClO_4)_4$ (**3**). Complex **3** consists of two terminal copper(II) units and a neutral $\{Ni(tap)_2\}$ moiety acting as a bis-monodentate bridging ligand to form a linear structure. The central nickel(II) ion is on an inversion center. In **3**, the tap$^-$ ligands bind to two metal ions in a $\kappa^1N{:}\kappa^2N$ bridging mode with local C_2 symmetry along the Ni−Cu axis. The nickel(II) ion is surrounded by four nitrogens from two tap$^-$ ligands, with Ni−N distances of 1.842(2) and 1.852(2) Å (Table 2), which are slightly longer than the values for tap$^-$ in **2** [1.837(3)−1.845(3) Å] and close to those of Htap in **1**. The Cu^{II} ions are in a trigonal-bipyramidal environment and the apical position of each Cu atom is occupied by the tertiary nitrogen from tren and N$_{central}$ from the tap$^-$ ligand, with a distance of 2.009(2) Å for the latter. The minus charge of each tap$^-$ ligand is localized on this nitrogen to bind the Cu atom, and, again, the terminal C−N bonds in the tap$^-$ ligands have double-bond character, with shorter distances [1.283(3) and 1.287(3) Å]. This charge localization causes a slight elongation of the Ni−N distances compared to those of the tap$^-$ ligands of **2a** and **2b**. Each N$_{terminal}$ is bound to an oxygen atom from a perchlorate ion by a hydrogen bonding [N(1)···O(8)′ = 2.987(3) and N(3)···O(7)′′ = 3.017(3) Å].

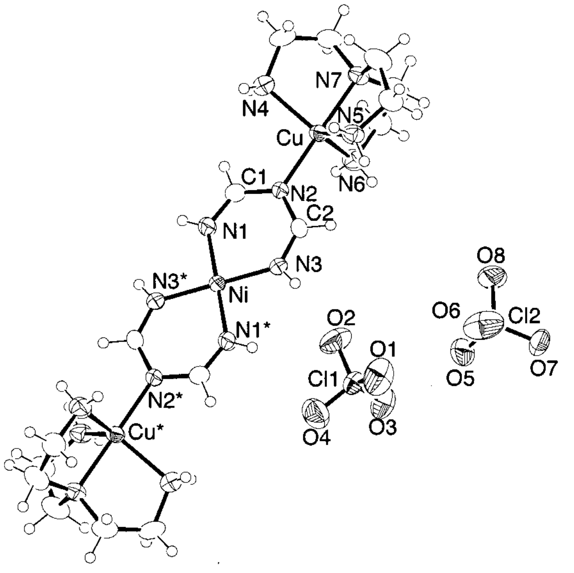


Figure 5. An ORTEP diagram of trinuclear complex **3** with 50% displacement ellipsoids; symmetry transformations used to generate equivalent atoms: * $-x + 1$, $-y$, $-z + 1$

Table 2. Selected bond lengths (Å) and angles (°) for complex **3**

Ni−N(1)	1.852(2)	Ni−N(3)	1.842(2)
Cu−N(2)	2.009(2)	Cu−N(5)	2.110(3)
Cu−N(4)	2.098(2)	Cu−N(6)	2.053(3)
Cu−N(7)	2.038(2)		
N(1)−C(1)	1.287(3)	C(1)−N(2)	1.344(3)
N(2)−C(2)	1.346(3)	C(2)−N(3)	1.283(3)
N(1)−Ni−N(3)	88.00(11)	N(1)*−Ni−N(3)[a]	92.00(11)
N(2)−Cu−N(7)	179.11(9)	N(2)−Cu−N(4)	96.28(9)
N(2)−Cu−N(5)	97.30(9)	N(2)−Cu−N(6)	94.87(9)
N(4)−Cu−N(5)	115.86(12)	N(4)−Cu−N(6)	117.65(13)
N(5)−Cu−N(6)	123.09(14)		

[a] Symmetry code: * $-x + 1$, $-y$, $-z + 1$.

Structure of Complex 4

Figure 6 shows the structure of multinuclear complex **4**. This complex consists of three independent complexes, dicationic $[Ni(Htap)_2]^{2+}$, including Ni1 (complex $\mathbf{4a^{2+}}$), dianionic dinuclear $[Ni(NCS)_5\{Ni(tap)(Htap)\}]^{2-}$, including Ni2 and Ni3 (complex $\mathbf{4b^{2-}}$), and neutral trinuclear $[Ni(NCS)_4\{Ni(tap)(Htap)\}_2]$, with Ni4 and Ni5 (complex **4c**). Ni5 in **4c** is located on a crystallographic inversion center, therefore complex **4** is formulated as $\mathbf{(4a)_2(4b)_2(4c)}$. The structure of dicationic $\mathbf{4a^{2+}}$ is similar to **1**, with longer Ni−N distances of 1.842(4)−1.858(4) Å and shorter $C-N_{terminal}$ distances of 1.250(6)−1.277(6) Å showing the double-bonding character of $C-N_{terminal}$ (Table 3). In $\mathbf{4b}^{2-}$, the complexed ligand $\{Ni(tap)(Htap)\}^+$ coordinates to an $\{Ni(NCS)_5\}^{3-}$ moiety through the $N_{central}$ of tap^- (N8) with a bond length of 2.086(3) Å. The $C-N_{terminal}$ distances are short [1.257(6)−1.286(5) Å] due to the localization of the negative charge on $N_{central}$. Trinuclear **4c** consists of an anionic $\{Ni(NCS)_4\}^{2-}$ and two complexed ligands coordinating through N19, with a distance of 2.1048(19) Å. The complexed ligands in **4c** show similar structural features to those in $\mathbf{4b^{2-}}$. Non-coordinating $\mathbf{4a^{2+}}$ and two $\{Ni(tap)(Htap)\}^+$ units from $\mathbf{4b^{2-}}$ and **4c** are arranged almost parallel to each other with close Ni···Ni contacts of 3.7764(10) Å from $\mathbf{4a^{2+}}$ to $\mathbf{4b^{2-}}$ and 3.3328(10) Å from $\mathbf{4b^{2-}}$ to **4c**. The positive charge repulsion between $Ni^{II}\cdots Ni^{II}$ centers is slightly diminished for the $\mathbf{4c/4b^{2-}}$ couple compared with $\mathbf{4a^{2+}/4b^{2-}}$.

Table 3. Selected interatomic distances(Å) for complex **4**

$4a^{2+}$	Ni(1)−N(1)	1.844(4)	Ni(1)−N(3)	1.858(4)
	Ni(1)−N(4)	1.848(4)	Ni(1)−N(6)	1.842(4)
	N(1)−C(1)	1.262(6)	C(1)−N(2)	1.351(6)
	N(2)−C(2)	1.348(5)	C(2)−N(3)	1.273(6)
	N(4)−C(3)	1.277(6)	C(3)−N(5)	1.335(6)
	N(5)−C(4)	1.359(6)	C(4)−N(6)	1.250(6)
$4b^{2-}$	Ni(2)−N(7)	1.828(3)	Ni(2)−N(9)	1.831(3)
	Ni(2)−N(10)	1.850(4)	Ni(2)−N(12)	1.853(4)
	N(7)−C(5)	1.286(5)	C(5)−N(8)	1.334(5)
	N(8)−C(6)	1.328(5)	C(6)−N(9)	1.285(5)
	N(10)−C(7)	1.267(5)	C(7)−N(11)	1.336(6)
	N(11)−C(8)	1.332(6)	C(8)−N(12)	1.257(5)
	Ni(3)−N(8)	2.086(3)	Ni(3)−N(13)	2.054(4)
	Ni(3)−N(14)	2.072(4)	Ni(3)−N(15)	2.080(3)
	Ni(3)−N(16)	2.065(3)	Ni(3)−N(17)	2.108(3)
4c	Ni(4)−N(18)	1.825(4)	Ni(4)−N(20)	1.839(3)
	Ni(4)−N(21)	1.856(4)	Ni(4)−N(23)	1.854(4)
	N(18)−C(14)	1.284(5)	C(14)−N(19)	1.330(5)
	N(19)−C(15)	1.336(5)	C(15)−N(20)	1.281(5)
	N(21)−C(16)	1.268(5)	C(16)−N(22)	1.361(5)
	N(22)−C(17)	1.339(5)	C(17)−N(23)	1.261(5)
	Ni(5)−N(19)	2.104(3)	Ni(5)−N(24)	2.071(4)
	Ni(5)−N(25)	2.075(4)		
	Ni(1)···Ni(2)	3.7763(11)	Ni(2)···Ni(4)	3.3329(11)

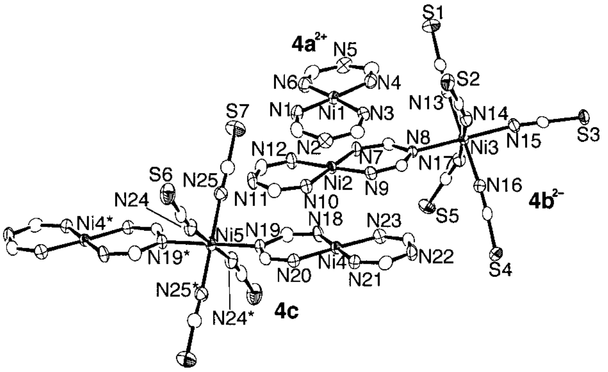


Figure 6. An ORTEP diagram of trinuclear complex **4** with 30% displacement ellipsoids; hydrogen atoms are omitted for clarity; symmetry transformations used to generate equivalent atoms: * $-x + 2$, $-y + 2$, $-z$

Conclusion

We have reported the decomposition reaction of triazine in the presence of nickel(II) to give Htap and tap^- complexes. $[Ni(Htap)_2]^{2+}$ and its deprotonated derivatives $[Ni(tap)(Htap)]^+$ and $[Ni(tap)_2]$ were obtained as mononuclear complexes for the former two and as complexed ligands for the latter two species. Two multinuclear complexes **3** and **4** contain the complexed ligands $[Ni(tap)_2]$ and $[Ni(tap)(Htap)]^+$ acting as a bridging ligand and as a terminal ligand, respectively. As expected, the tap^- ligand bridges two metal ions in a $\kappa^1N{:}\kappa^2N$ mode with local C_2 symmetry. The formation of a new complexed ligand should be possible with Htap, which can act as a ferromagnetic coupler like $[Cu(bptap)_2]$. Such investigations are now in progress in our laboratory.

Experimental Section

Synthesis of $[Ni(Htap)_2](ClO_4)_2$ (1): A solution of nickel(II) perchlorate hexahydrate in ethanol (0.1 M, 5 mL) and triazine in methanol (0.2 M, 5 mL) were mixed and the resulting pale-green solution was heated to 50 °C for 2 hours, during which time the solution turned yellow. Upon standing overnight, yellow crystals formed. Yield 130 mg (65%). $C_4H_{10}Cl_2N_6NiO_8$ (399.8): calcd. C 12.02, H 2.52, N 21.02; found C 12.17, H 2.71, N 20.87.

Synthesis of $[Ni(tap)(Htap)]ClO_4\cdot H_2O$ ($2\cdot H_2O$): Three 0.2 M solutions of nickel(II) perchlorate/EtOH (1 mL), ethylenediamine/EtOH (2 mL), and triazine/MeOH (1 mL) were mixed and the resulting blue solution was heated to 70 °C for 1 hour to afford a blue solution. The yellow fraction isolated by column chromatography (Sephadex LH-20/EtOH) was dried. The resulting compound was recrystallized from EtOH/H_2O (1:1, v/v) to give yellow crystals of $\mathbf{2}\cdot H_2O$. Yield 11 mg (35%). $C_4H_{11}ClN_6NiO_5$ (317.3): calcd. C 15.14, H 3.49, N 26.48; found C 15.18, H 3.46, N 26.37.

Synthesis of $[\{Cu(tren)\}_2\{Ni(tap)_2\}](ClO_4)_4$ (3): A yellow suspension of $\mathbf{2}\cdot H_2O$ (3.4 mg, 0.011 mmol) in EtOH/H_2O (1:1, v/v; 1 mL) was added to $[Cu(tren)]ClO_4$ (8.2 mg, 0.027 mmol) in EtOH/H_2O (1:1, v/v; 1 mL). The mixture was stirred to afford a blue-green solution. Blue-green crystals of **3** were obtained from this solution after several days. Yield 6.7 mg (60%). $C_{16}H_{44}Cl_4Cu_2N_{14}NiO_{16}$ (1016.2): calcd. C 18.91, H 4.36, N 19.30; found C 19.10, H 4.45, N 19.21.

Synthesis of $[Ni(Htap)_2]_2[Ni(2)_2(NCS)_4][Ni(2)(NCS)_5]_2\cdot 8H_2O$ ($4\cdot 8H_2O$): A solution of $\mathbf{2}\cdot H_2O$ (12 mg, 0.038 mmol) in EtOH/ H_2O (1:1, v/v; 1 mL) was added to 0.2 mL of 0.1 M nickel(II) perchlorate/ EtOH solution and 0.8 mL of a 0.1 M NH_4SCN/MeOH solution,

Table 4. Crystallographic data and structural refinement for **1−4**

Complex	**1**	**2**·H_2O	**3**	**4**·$8H_2O$
Enpirical formula	$C_4H_{10}Cl_2N_6NiO_8$	$C_4H_{11}ClN_6NiO_5$	$C_{16}H_{44}Cl_4N_{14}NiCu_2O_{16}$	$C_{38}H_{72}N_{50}Ni_9O_8S_{14}$
Molecular mass	399.77	317.32	1016.22	2334.47
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (Å)	5.1543(7)	9.3000(16)	9.6351(12)	10.759(3)
b (Å)	9.0810(12)	10.3129(18)	14.7930(18)	11.110(3)
c (Å)	13.5606(18)	12.949(2)	13.0565(16)	20.223(6)
α (°)		74.855(3)		77.971(7)
β (°)	91.997(3)	81.322(3)	95.619(4)	83.374(8)
γ (°)		63.411(3)		70.152(7)
V (Å^3)	634.33(15)	1071.2(3)	1852.0(4)	2221.3(10)
Z	2	4	2	1
T (K)	200(2)	210(2)	223(2)	223(2)
ρ_{calc} (g cm^{-3})	2.093	1.968	1.822	1.745
Reflections collected	5074	10340	13075	22593
Independent reflections	1760 [R_{int} = 0.023]	4699 [R_{int} = 0.030]	4257 [R_{int} = 0.031]	10187 [R_{int} = 0.046]
μ (mm^{-1})	2.004	2.084	2.014	2.264
R_1, wR_2 [$I > 2\sigma(I)$]	0.032, 0.075	0.042, 0.098	0.033, 0.0631	0.040, 0.066
R_1, wR_2 (all data)	0.043, 0.078	0.050, 0.102	0.053, 0.066	0.097, 0.073

and the resulting yellow solution was allowed to evaporate slowly in air. After a week, green crystals of **4**·$4H_2O$ were obtained which were collected by filtration and dried in vacuo. Yield 4.2 mg (30%). $C_{38}H_{56}N_{50}Ni_9S_{14}$ (2190.3): calcd. C 20.90, H 2.59, N 32.09; found C 20.76, H 2.67, N 32.33.

X-ray Crystallography: Data for all the compounds were collected on a Bruker SMART APEX diffractometer employing graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at low temperature (200−233 K). The data integration and reduction were undertaken with SAINT and XPREP.[13] An empirical absorption correction determined with SADABS[14] was applied to each data set. The structures were solved by direct methods using SHELXS-97[15] and refined using least-squares methods on F^2 with SHELXL-97.[15] Non-hydrogen atoms were modelled with anisotropic displacement parameters, and hydrogen atoms were placed by difference Fourier syntheses and refined isotropically. Further details can be found in Table 4.

CCDC-230135−230138 (**1−4**)contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/ conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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