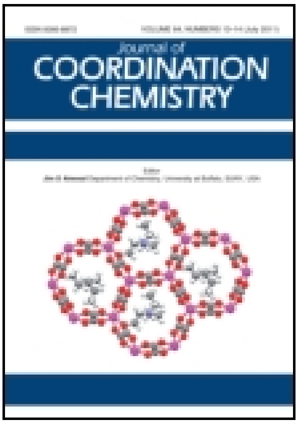

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Structural diversity in trinuclear nickel(II) complexes of 3,5-diamino-1,2,4-triazole

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Structural diversity in trinuclear nickel(II) complexes of 3,5-diamino-1,2,4-triazole

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Two trinuclear 3,5-diamio-1,2,4-triazole(Hdatz)-derived nickel(II) compounds, $[Ni_3(Hdatz)_6(H_2O)_6]Br_6 \cdot 4H_2O$ (**1**) and $[Ni_3(Hdatz)_6(datz)_2(H_2O)_4]Cl_4 \cdot 6H_2O$ (**2**), are reported. Structural analyses reveal that in **1** the six Hdatz ligands are bidentate N1, N2-bridging coordination. However, the X-ray diffraction analysis shows that in **2** there are eight triazole ligands, six of which are neutral and two deprotonated. Four neutral triazoles are N1, N2-bridging and two monodentate; the deprotonated triazoles (datz) are bidentate N1, N2-bridging. The coexistence of both neutral and anionic triazole ligands as well as different coordination modes in one compound is relatively rare. The difference in coordination modes is believed to be anion-controlled. Both compounds are additionally characterized by elemental analysis, IR, and UV-Vis spectroscopy.

Keywords: 3,5-Diamino-1,2,4-triazole; Nickel(II) compound; Crystal structure; Structural diversity

1. Introduction

Design and synthesis of metal-organic complexes have flourished because of their intriguing architectures [1] and potential applications to gas storage, ion exchange, catalysis, optics, and magnetism [2]. Although a large number of complexes with intriguing structures and physical properties have been reported, structure function correlations within these materials still remains a challenge in coordination chemistry and crystal engineering [3]. Skillful selection of appropriate ligands and metal ions is pivotal for preparing complexes with desired properties.

1,2,4-Triazole and its derivatives have potential bridging (μ1,2, μ2,4, and μ1,2,4) and in few cases monodentate coordination (N4) [4]. Many triazole-based polynuclear

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compounds have been reported, including dinuclear, linear trinuclear, cyclic trinuclear, and hexanuclear ring complexes [5]. 3,5-Dimino-1,2,4-triazole (Hdatz) has been known and a number of its metal complexes were investigated, some structurally characterized by single-crystal X-ray diffraction [6]. Our interest focused on high-nitrogen energetic materials, particularly energetic coordination compounds [7]. Since Hdatz contains rich nitrogen atoms and its metal complexes could be potential energetic materials, we prepared a number of complexes derived from Hdatz. In order to establish the coordination sphere at the metal, crystal structure determinations were undertaken. Nickel compounds derived from Hdatz have similar crystal structures except with Cl^- as counter ion. Herein, we report two trinuclear nickel(II) compounds derived from 3,5-diamino-1,2,4-triazole, $[Ni_3(Hdatz)_6(H_2O)_6]Br_6 \cdot 4H_2O$ (**1**) and $[Ni_3(Hdatz)_6(datz)_2(H_2O)_4]Cl_4 \cdot 6H_2O$ (**2**). In the molecular structure of **2**, 3,5-diamino-1,2,4-triazole has both neutral and anionic forms, a rare occurrence; **1** with Br^- as counter ion has usual μ1,2 coordination similar to reported trinuclear nickel(II) compounds with SO_4^{2-}, NO_3^-, SCN^- or SiF_6^{2-} as counter ions [6a,6e,6f].

2. Experimental

2.1. *Materials and physical measurements*

3,5-Diamino-1,2,4-triazole was purchased from Aldrich and used as received. Other reagents are of analytical grade and used without purification.

IR spectra of the complexes were recorded on a Perkin Elmer FT-IR spectrophotometer from 4000 to 400 cm^{-1} using KBr pellets. Elemental contents of carbon, hydrogen, and nitrogen were determined by a German Vario EL III analyzer. The crystal structure was determined with a Bruker Smart-1000 CCD diffractometer. UV-Vis spectra were performed on a TU-1901 UV-Vis spectrophotometer.

2.2. *Synthesis*

2.2.1. $[Ni_3(Hdatz)_6(H_2O)_6]Br_6 \cdot 4H_2O$ (1). A 20 mL ethanol solution of $NiBr_2 \cdot 3H_2O$ (0.1363 g, 0.5 mmol) was added dropwise to a hot 20 mL ethanol solution of Hdatz (0.099 g, 1.0 mmol) under stirring. The resulting blue precipitate was collected after stirring at 60°C for another 1 h and washed with 5 mL ethanol three times. The precipitate was dried in air. Yield: 0.149 g (52.1%). Elemental Anal. Calcd (%): C, 10.08; H, 3.52; N, 29.38. Found: C, 10.21; H, 3.78; N, 28.57. FT-IR (KBr, cm^{-1}): 3458, 3331, 1620, 1510, 1448, 1261, 1043, 827, 572, 526, 447.

2.2.2. $[Ni_3(Hdatz)_6(datrz)_2(H_2O)_4]Cl_4 \cdot 6H_2O$ (2). A similar synthetic procedure to **1** was employed and $NiCl_2 \cdot 6H_2O$ was used instead of $NiBr_2 \cdot 3H_2O$. Yield: 0.063 g (24.4%). Elemental Anal. Calcd (%): C, 14.91; H, 4.54; N, 43.47. Found: C, 15.20; H, 4.26; N, 44.38. FT-IR (KBr, cm^{-1}): 3392, 3313, 3219, 3166, 1641, 1517, 1448, 1379, 1039, 865, 815, 675, 563.

Table 1. Crystal and structure refinement data for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{12}H_{50}Ni_3N_{30}Br_6O_{10}$	$C_{16}H_{58}Ni_3N_{40}Cl_4O_{10}$
Molecular mass	1430.41	1288.79
Crystal size (mm^3)	0.20 × 0.18 × 0.11	0.39 × 0.26 × 0.13
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	9.880(10)	9.4452(19)
b	12.122(13)	10.485(2)
c	12.44(2)	13.663(3)
α	104.60(2)	105.624(5)
β	106.88(2)	104.662(4)
γ	110.523(16)	91.441(6)
Volume (Å^3), Z	1227(3), 1	1254.3(4), 1
Calculated density (g cm^{-3})	1.937	1.706
$F(000)$	706	666
θ range for data collection	1.86–26.00	2.38–25.50
Reflections collected/unique	3778/2681 [R(int) = 0.0258]	9646/4648 [R(int) = 0.0129]
Goodness-of-fit on F^2	1.092	1.036
Final R indices [I > $2\sigma(I)$]	$wR_2 = 0.2190$ $wR_2 = 0.0642$	$R_1 = 0.0770$, $R_1 = 0.0246$,
R indices (all data)	$wR_2 = 0.2439$ $wR_2 = 0.0663$	$R_1 = 0.1111$, $R_1 = 0.0276$,
Largest difference peak and hole (e · nm^{-3})	2.657 and −1.302	0.369 and −0.397

2.3. *X-ray diffraction analysis*

Single crystals of both compounds suitable for X-ray diffraction analysis were obtained by slow evaporation of their aqueous solution for 3 weeks. A single crystal of each compound was coated with epoxy glue in order to prevent spontaneous liberation of solvent molecules under ambient conditions. The determination of the unit cell and the data collection for the complexes were performed on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using phi and omega scans technique. The structures were solved by direct methods and refined on F^2 by full matrix least-squares with Bruker's SHELXL-97 program [8]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated using a riding model. Data collection details and structure determination results are summarized in table 1. Selected bond lengths and angles as well as hydrogen bonds are presented in tables 2 and 3. The final R indices for **1** are moderately high probably because of the statistical disorder of organic amines and poor crystal quality.

3. Results and discussion

3.1. *Crystal structures*

3.1.1. $[Ni_3(Hdatz)_6(H_2O)_6]Br_6 \cdot 4H_2O$ (1). The trinuclear cation of **1** (figure 1) has six 3,5-diamino-1,2,4-triazole (Hdatz) ligands, each bridging two nickels. The central nickel

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

1		**2**	
Ni(1)–N(1)	2.096(9)	Ni(1)–N(1)	2.0934(15)
Ni(1)–N(12)	2.029(10)	Ni(1)–N(11)	2.1098(15)
Ni(1)–N(6)	2.068(10)	Ni(1)–N(6)	2.1306(15)
Ni(1)–N(11)	2.102(9)	Ni(2)–O(1)	2.1381(14)
Ni(2)–N(2)	2.037(10)	Ni(2)–O(2)	2.1701(14)
Ni(2)–N(7)	2.054(8)	Ni(2)–N(2)	2.0619(15)
Ni(2)–O(1W)	2.120(9)	Ni(2)–N(7)	2.0837(16)
Ni(2)–O(2W)	2.079(9)	Ni(2)–N(12)	2.0859(15)
Ni(2)–O(3W)	2.112(7)	Ni(2)–N(16)	2.0938(16)
N(6)–Ni(1)–N(6B)	180.000(2)	N(1)–Ni(1)–N(11)	91.57(6)
N(6)–Ni(1)–N(1)	90.9(4)	N(1)–Ni(1)–N(11A)	88.43(6)
N(6)–Ni(1)–N(1B)	89.1(4)	N(1)–Ni(1)–N(6)	91.95(6)
N(1)–Ni(1)–N(1B)	180.0(5)	N(1)–Ni(1)–N(6A)	88.05(6)
N(11)–Ni(1)–N(1)	90.9(3	N(11)–Ni(1)–N(6)	90.83(6)
N(11)–Ni(1)–N(1B)	89.1(3)	N(11)–Ni(1)–N(6A)	89.17(6)
N(2)–Ni(2)–N(12)	94.0 (4)	N(2)–Ni(2)–N(7)	94.01(6)
N(7)–Ni(2)–N(12)	93.9(4)	N(2)–Ni(2)–N(12)	94.81(6)
N(7)–Ni(2)–N(2)	92.0(4)	N(7)–Ni(2)–N(12)	92.43(6)
N(2)–Ni(2)–O(3W)	86. 8(3)	N(2)–Ni(2)–N(16)	92.55(6)
N(12)–Ni(2)–O(3W)	88.3(4)	N(16)–Ni(2)–N(7)	171.29(6)
N(2)–Ni(2)–O(2W)	93.8(4)	N(12)–Ni(2)–N(16)	92.74(6)
N(12)–Ni(2)–O(2W)	171.3(3)	N(2)–Ni(2)–O(1)	86.98(6)
O(2W)–Ni(2)–O(3W)	88.1 (3)	N(7)–Ni(2)–O(1)	88.45(6)
N(7)–Ni(2)–O(2W)	89.9 (4)	N(2)–Ni(2)–N(7)	94.01(6)
N(7)–Ni(2)–O(1W)	91.8(4)	N(12)–Ni(2)–O(1)	177.95(5)
N(7)–Ni(2)–O(3W)	177.6(4)	N(16)–Ni(2)–O(1)	86.16(6)
N(2)–Ni(2)–O(1W)	175.3(3)	N(16)–Ni(2)–O(2)	87.93(6)
N(12)–Ni(2)–O(1W)	88.6(4)	N(7)–Ni(2)–O(2)	84.98(6)
O(2W)–Ni(2)–O(1W)	83.3 (3)	N(2)–Ni(2)–O(2)	174.33(6)
O(1W)–Ni(2)–O(3W)	894 (3)	N(12)–Ni(2)–O(2)	90.82(6)
		O(1)–Ni(2)–O(2)	87.41(6)

Symmetry operation: A: $-x$, $-y$, $-z$; B: $-x+1$, $-y+1$, $-z+1$.

Table 3. Selected hydrogen bonds and angles for **1** and **2**.

Compound	Atoms	Distances (Å)	Angles (°)
$[Ni_3(Hdatz)_6(H_2O)_6]Br_6\cdot 8H_2O$ (**1**)	O(2W)–H(2WB)···O(4W)i	3.759, 1.81	168
	N(3)–H(3A)···Br(1)i	3.443, 2.74	140
	O(3W)–H(3WB)···O(4W)i	3.359, 2.45	158
	N(5)–H(5B)···Br(1)i	3.393, 2.63	148
	N(8)–H(8A)···N(15)ii	3.309, 2.60	140
	N(8)–H(8A)···Br(1)iii	3.380, 2.67	140
	N(9)–H(9B)···Br(1)iii	3.381, 2.63	147
	N(10)–H(10B)···N(15)ii	3.249, 2.46	152
	N(13)–H(13A)···Br(3)iv	3.395, 2.65	145
	N(14)–H(14B)···Br(3)iv	3.562, 2.82	146
$[Ni_3(Hdatz)_6(datrz)_2(H_2O)_4]Cl_4\cdot 6H_2O$ (**2**)	N(19)–H(19)B···Cl(2)i	3.325, 2.52	155
	N(20)–H(20B)···N(3)ii	2.998, 2.13	168
	N(17)–H(17)···Cl(1)	3.325, 2.56	170
	N(15)–H(15B)···Cl(2)iii	3.343, 2.56	152
	N(14)–H(14B)···N(3)iv	3.058, 2.22	166
	N(13)–H(13)···N(5)iv	2.877, 2.02	176
	N(10)–H(10B)···N(4)v	3.172, 2.35	164
	N(4)–H(4B)···O(3)vi	3.190, 2.44	155

Symmetry transformations used to generate equivalent atoms: for **1** i: $1-x$, $1-y$, $1-z$; ii: $-1+x$, y, z; iii: $-x$, $-y$, $1-z$; iv: $\underline{x}$, y, $1+z$; for **2** i: $-x+1$, $-y+1$, $-z+1$; ii: $-x$, $-y+1$, $-z$; iii: $-x+1$, $-y$, $-z$; iv: $x+1$, y, z; v: x, $y-1$, z; vi: $x-1$, y, z.

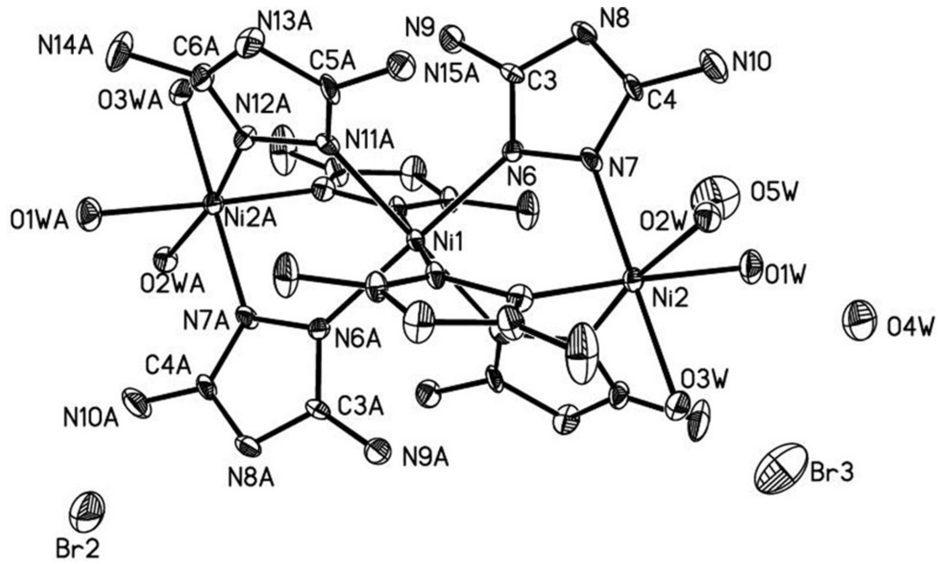

Figure 1. ORTEP diagram (at 30% probability) of $[Ni_3(Hdatz)_6(H_2O)_6]Br_6 \cdot 4H_2O$ (**1**). Hydrogen atoms are omitted for clarity.

is connected to six nitrogen atoms of Hdatz in an octahedral geometry while the terminal nickel atoms lie on special positions (of 3 site symmetry), coordinated by three nitrogen atoms of Hdatz and three water molecules. The structure of the cation of **1** is similar to those of two trinuclear nickel compounds we reported earlier [6e, 6i] and analogs in the literature [6a, 6g, 6h]. The two unique Ni–N bond distances (Ni1–N1 = 2.096(9) and Ni2–N2 = 2.036(10)) are significantly different from each other, and the bond lengthening around Ni1 may be influenced to some extent by the crystal packing of six bulky ligands. The Ni–N distances are very close to those found earlier: 2.093(3)–2.127(3) Å in $Ni_3(SCN)_6(Hdatz)_6 \cdot 6H_2O$ [6h], 2.059(2)–2.108(3) Å in $[Ni_3(Hdatz)_6(H_2O)_6](SO_4)_3 \cdot H_2O$ [6e] and 2.062(2)–2.111(2) Å in $[Ni_3(Hdatz)_6(H_2O)_6](SiF_6)_3 \cdot 20H_2O$ [6i]. Distortion from ideal octahedral geometry of the coordination polyhedron involves only the bond angles, whose deviations are large around the terminal Ni's (maximum 8.7°), while the coordination geometry around the central Ni is with a nearly ideal octahedron. Adjacent Ni–Ni distance within the trinuclear molecule is 3.680(8) Å, shorter than those (3.831(3) and 3.737(3) Å) observed in $Ni_3(SCN)_6(Hdatz)_6 \cdot 6H_2O$ and $[Ni_3(Hdatz)_6(H_2O)_6](NO_3)_6 \cdot 2H_2O$, respectively. The triazole rings are planar within experimental error. Bond distances and angles of the ring compare well with those found in other analogs [6]. There are rich intra- and inter-molecular hydrogen bonds, N(5)–H(5B)···Br(1)i, N(8)–H(8A)···N(15)ii, and O(2W)–H(2WB)···O(4W)i (i: $1-x$, $1-y$, $1-z$; ii: $-1+x$, y, z) (details shown in figure 3) between Hdatz ligands, coordinated water molecules, Br^-, and crystalline water molecules; O5W is found to be disordered and the possible reason is the disorder occupancy of the water molecule.

3.1.2. $[Ni_3(Hdatz)_6(datz)_2(H_2O)_4]Cl_4 \cdot 6H_2O$ (2).

X-ray crystallographic analysis reveals that **2** crystallizes in the triclinic *P*-1 space group, similar to that of **1**.

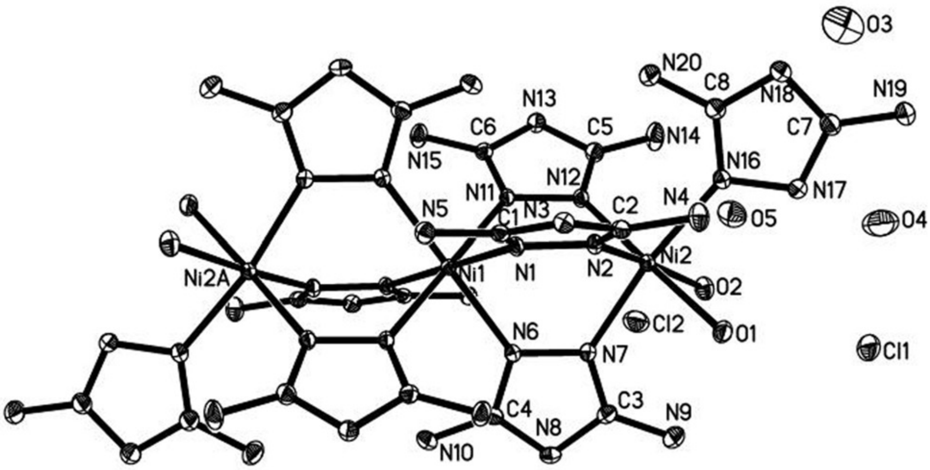

Figure 2. ORTEP diagram (at 30% probability) of $[Ni_3(Hdatz)_6(datz)_2(H_2O)_4]Cl_4 \cdot 6H_2O$ (**2**). Hydrogen atoms are omitted for clarity.

As shown in figure 2, **2** has six neutral 3,5-diamino-1,2,4-triazole ligands, four of which are bridging and two are terminal. Another two bridging ligands are deprotonated. The central nickel, as the inversion center, is connected to six nitrogen atoms of four neutral ligands and two anionic ligands in an octahedral geometry. The terminal nickel atoms lie also on special positions (of 3 site symmetry), coordinated by three nitrogen atoms of neutral Hdatz, two water molecules and one nitrogen atom of an anionic ligand. The existence of both neutral and deprotonated forms of Hdatz in one molecule is very rare; one example is $[Co_3(dat)_4(datH)_2(H_2O)_6]Cl_3 \cdot 9H_2O$ (datH = 3,5-diamino-1,2,4-triazole and dat is its deprotonated form), where the central cobalt is +III and the two terminal cobalts are +II, and the counter ion is also Cl^- [6g]. It is unclear why two Hdatz ligands are deprotonated during coordination with nickel(II) when $NiCl_2 \cdot 6H_2O$ is used instead of $NiBr_2 \cdot 3H_2O$. We have previously prepared analogs with SO_4^{2-} or SiF_6^- as counter anions, the crystal structures of their cations and that of **1** are identical, thus we postulated that the smaller ionic radii of Cl^- is at least partly responsible for its different coordination modes and tried to grow single crystals of its counterpart with F^- as counter ion. Unfortunately, we always collected pale green powders and could not determine its crystal structure. Nevertheless, we believed that the coordination modes of Hdatz are anion-controlled, as encountered in some cases [4b, 5d].

The Ni–N bond distances (Ni1–N6 = 2.13066(15), Ni2–N7 = 2.0837(16), and Ni1–N1 = 2.0934(15) Å) are significantly different from each other, as found in **1**. The Ni–O bond distances (Ni2–O1 = 2.1381(14) and Ni2–O2 = 2.1701(14) Å) are considerably longer than those in **1** (Ni2–O1 = 2.119(9), Ni2–O2 = 2.079(9), and Ni2–O3 = 2.113(7) Å). The N–N bond distances in deprotonated ligands are shorter than those in neutral bridging ligands, and the C–N bond (adjacent to the NN bond) lengths are shorter than those found in neutral ones. The coordination geometry around the central Ni is a nearly ideal octahedron, as in **1**; the maximum deviation of the coordination geometry from the ideal geometry around the terminal nickels is also 8.7°. Adjacent Ni–Ni distance within the trinuclear molecule is 3.728(8) Å, longer than that observed in **1**. There also exist rich intra- and intermolecular hydrogen bonds,

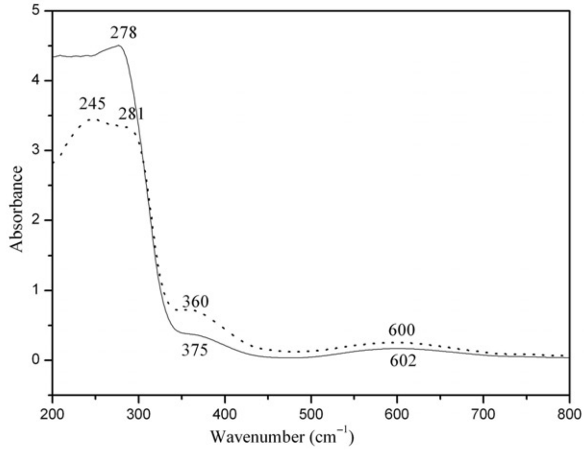

Figure 3. UV-Vis spectra of two trinuclear nickel compounds in methanol: (——), **1** and (……), **2**.

N(19)–H(19)B $\cdots$ Cl(2)i, N(20)–H(20B) $\cdots$ N(3)ii, and N(4)–H(4B) $\cdots$ O(3)vi (i: $-x+1$, $-y+1$, $-z+1$; ii: $-x$, $-y+1$, $-z$; vi: $x-1$, y, z) (details shown in figure 3) between Hdatz, datz, coordinated water, Cl$^-$, and crystalline water.

3.2. *Spectral studies*

The UV spectrum of **1**, as shown in figure 3, showed absorptions of Hdatz in the ultraviolet region at 278 and 375 nm due to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions and of Ni(II) at 602 nm ascribed to $d \rightarrow d$ transition. Correspondingly, in **2**, as depicted also in figure 3, the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the Hdatz ligand are at 281 and 360 nm, respectively, and the $d \rightarrow d$ transition of Ni(II) is at 600 nm; an additional absorption at 245 nm is tentatively assigned to the $\pi \rightarrow \pi^*$ transition of deprotonated triazole. IR spectra of both compounds showed broad and strong peaks of N–H and O–H stretching vibrations between 3460 and 3200 cm^{-1} and very strong peaks of N–H bend between 1640–1620 cm^{-1}, in addition to peaks attributable to C=N stretching vibrations at 1517 and 1448 cm^{-1} for **1** and 1510 and 1446 cm^{-1} for **2**. The shift of C=N stretching frequencies in the coordinated ligand compared with free Hdatz (1487 and 1409 cm^{-1}) indicates that Hdatz adopt N1, N2-bridging coordination.

4. Conclusion

We have synthesized two new trinuclear Ni(II) compounds derived from 3,5-diamino-1,2,4-triazole. Crystal structure analyses revealed that each compound has an inversion center located on the central nickel, which is coordinated by six nitrogen atoms defining a nearly ideal octahedron. In contrast to the usual coordination pattern of Hdatz in **1** with Br$^-$ as counter ion, in **2**, with Cl$^-$ as counter ion, Hdatz ligands adopt both bidentate N1,N2-bridging and monodentate N1/N2 coordination; two triazole ligands are deprotonated and bidentate N1,N2-bridging ligands. The coexistence of neutral and deprotonated Hdatz ligands and its monodentate and bidentate coordination modes in one complex is rare. The difference in coordination modes in these two compounds is believed to be anion-controlled.

Supplementary material

CCDC-825015 (**1**) and CCDC-825035 (**2**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033; E-mail: deposit@ccdc.cam.ac.uk.

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