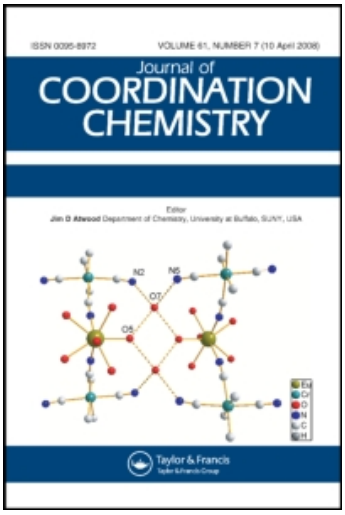

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Structural, infrared spectral and thermogravimetric analysis of a hydrogen-bonded assembly of cobalt(II) and nickel(II) mixed complex cations with hexamethylenetetraamine and aqua ligands: $\{[M(hmt)_2(H_2O)_4][M(H_2O)_6]\}(SO_4)_2 \cdot 6H_2O$

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STRUCTURAL, INFRARED SPECTRAL AND THERMOGRAVIMETRIC ANALYSIS OF A HYDROGEN-BONDED ASSEMBLY OF COBALT(II) AND NICKEL(II) MIXED COMPLEX CATIONS WITH HEXAMETHYLENETETRAAMINE AND AQUA LIGANDS: $\{[M(hmt)_2(H_2O)_4][M(H_2O)_6]\}(SO_4)_2 \cdot 6H_2O$

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The synthesized cobalt(II) and nickel(II) complexes $\{[M(hmt)_2(H_2O)_4][M(H_2O)_6]\}(SO_4)_2 \cdot 6H_2O$ [M = Co(II) (**1**) and Ni(II) (**2**), hmt = hexamethylenetetraamine] share the same general formula and chemical name {[bis(hexamethylenetetraamine)tetraaquametal(II)][hexaaquametal(II)]} disulfate hexahydrate. Complexes **1** and **2** have been characterized by elemental analysis, infrared spectroscopy, thermal analysis and magnetic moment determination. Each complex has two different cationic complexes co-crystallizing with the sulfate anions. The crystal structure of **1** has been determined. Both complex cations in **1** have distorted octahedral geometry and they are linked to the sulfate anions through the coordinated and lattice water molecules. Each sulfate anion is hydrogen bonded to ten water molecules; two of its oxygen atoms have two hydrogen bonds each while the other two oxygen atoms have three hydrogen bonds each. The three uncoordinated nitrogen atoms of hmt in each $[Co(hmt)_2(H_2O)_4]^{2+}$ cation are hydrogen bonded to water molecules of adjacent $[Co(H_2O)_6]^{2+}$ cations. The thermal decomposition of **1** has been investigated further by analyzing the FTIR spectra of the residues formed from each decomposition step, and the data have contributed to establishing the thermal decomposition pathway of both **1** and **2**.

Keywords: Mixed cationic complexes; Cobalt(II); Nickel(II); Hexamethylenetetraamine; TG-DTA

INTRODUCTION

The hexamethylenetetraamine (hmt) molecule has four nitrogen atoms, each of which has a lone pair of electrons. Therefore, it is not surprising that hmt can provide

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donor sites for hydrogen bonding, and can act as a monodentate or bridging ligand. This is shown by its participation in metal(II) salt adducts, where the hmt is merely hydrogen bonded in the crystal lattice [1,2], in coordination polymers of various architectures [3,4], in inclusion compounds with hmt as host molecule [5], and in hydrogen-bonded assemblies of organic solids [6]. New inorganic and organic compounds containing hmt will therefore continue to attract the attention of researchers. Furthermore, these compounds can provide useful information on hydrogen-bonding effects on a variety of properties such as infrared spectral data, type of crystal structure and thermal stability [7]. This paper reports the synthesis, magnetic moment, spectral and thermogravimetric analysis of $\{[M(hmt)_2(H_2O)_4][M(H_2O)_6]\}(SO_4)_2 \cdot 6H_2O$ [M = Co(II), Ni(II)], and each of these complexes comprises two different cationic complexes co-crystallizing with the sulfate anions. The crystal structure of the cobalt(II) complex (**1**) shows an extensive hydrogen-bonding network interconnecting its constituent components and can be considered a hydrogen-bonded assembly.

EXPERIMENTAL

Synthesis of 1 and 2

All reagents were used as received. A mixture of $CoSO_4 \cdot 7H_2O$ (2.8 g, 0.01 mol), β-alanine (2.67 g, 0.03 mol) and 37% aqueous formaldehyde (15 mL, 0.18 mol) was stirred thoroughly. The pH of this solution was raised to 9.0 by adding concentrated ammonia. During the addition, the reaction mixture was cooled in ice water and was stirred constantly. The resultant solution was filtered. On standing at room temperature, the wine-red filtrate yielded hexagonal pink crystals suitable for X-ray crystal structure analysis. Yield: 1.1 g (25% based on $CoSO_4$). Anal. Calcd. for $Co_2C_{12}H_{56}N_8O_{24}S_2$(%): C, 16.40; H, 6.42; N, 12.76. Found: C, 16.01; H, 6.35; N, 12.59.

Compound **1** could also be synthesized by heating an aqueous mixture of cobalt sulfate heptahydrate (1.37 g, 0.0048 mol) and hexamine (0.68 g, 0.0048 mol) in a water bath at *ca* 60°C for about 30 min. The mixture was then filtered to remove the purple precipitate formed. Slow evaporation of the resultant filtrate yielded pink hexagonal crystals. The yield (0.91 g) was similar to the first method, about 21%. This method was used for making the nickel analogue **2**; the yield was 38% (based on $NiSO_4$). Anal. Calcd. for $Ni_2C_{12}H_{56}N_8O_{24}S_2$(%): C, 16.49; H, 6.46; N, 12.82. Found: C, 16.24; H, 6.35; N, 12.32.

Physical Measurements

C, H and N microanalysis was carried out with a Perkin Elmer 2400 instrument. Thermal analysis was performed on 10–22 mg samples using a Mettler Toledo Star System. Each sample was heated from 50 to 900°C under a nitrogen atmosphere flowing at 20 mL min^{-1}. The heating rate was set at 10°C min^{-1}. The residue at a given temperature T°C was obtained by heating a sample under the same conditions except the heating temperature range was 50 to T°C. Infrared spectra of the compounds were recorded as KBr pellets using a Nicolet-Magna-IR spectrometer in the frequency range 4000–600 cm^{-1}. Magnetic susceptibilities of **1** and **2** at room temperature were

determined by using a Sherwood Magnetic Susceptibility Balance MSB Mk1 that was calibrated with $Hg[Co(SCN)_4]$.

X-ray Crystallography

The diffraction data for **1** were collected on a Siemens CCD area-detector diffractometer at 168 K for a crystal $0.50 \times 0.39 \times 0.26$ mm using the ω-scan technique. Lorentz-polarization and absorption corrections were applied [8]. The structure was solved and refined by using SHELXS-97 and SHELXL-97, respectively [9,10]. The structure was refined from 7439 reflections ($R_{int} = 0.036$) to a low R index. However, the difference Fourier map showed two large peaks at (0.04, 0.45, 0.20) and (0.50, 0.04, 0.30). Although the checking program, PLATON [11], suggested that the voids were large enough to be occupied by water molecules, the refinement of the two peaks as oxygen atoms led to unacceptably large temperature factors. The CHN elemental percentages did not support the inclusion of a water molecule in the formula. The peaks were then removed by the SQUEEZE [12] option in the WinGX suite [13]; the removal also averaged equivalent reflections, so that the R_{int} was now zero. The water hydrogen atoms were then located and refined.

Crystal data, selected bond lengths and angles and hydrogen-bonding parameters are listed in Tables I–III. Complete lists of bond lengths and bond angles, and other crystal data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 200370. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge

TABLE I Crystal data and structure refinement details for **1**

Formula	$Co_2C_{12}H_{56}N_8O_{24}S_2$
Formula weight	878.63
Crystal system	Triclinic
Space group	$\bar{P}_1$
a (Å)	9.2631(7)
b (Å)	13.417(1)
c (Å)	15.978(1)
α (°)	66.137(1)
β (°)	89.178(1)
γ (°)	89.379(1)
λ (Å)	0.71073
V (Å^3)	1815.8(2)
D_c (g cm^{-3})	1.607
$F(000)$	924
μ	1.123
Z	2
Transmission factors	0.6037–0.758
2θ range (°)	3.4–53.2
Index ranges	$-11 \le h \le 11$; $-15 \le k \le 16$; $0 \le l \le 20$
Reflections	7345
Data [$F_o > 4\sigma(F_o)$]	5224
Goodness-of-fit on F^2	0.862
R	0.036
R_w	0.062
Weight (a)[a]	0.0323
Largest diff. peak, hole	0.333, −0.542

[a] $a_w = 1/[\sigma^2(F_o^2) + (aP)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

TABLE II Selected bond lengths (Å) and angles (°) for **1**

Co1–O1w	2.060(1)	O1w–Co1–O2w	93.9(1)
Co1–O1w	2.060(1)	O1w–Co1–O2w	86.1(1)
Co1–O2w	2.055(1)	O1w–Co1–N1	89.6(1)
Co1–O2w	2.055(1)	O1w–Co1–N1	90.4(1)
C1–N1	2.354(2)	O1w–Co1–O2w	86.1(1)
Co1–N1	2.354(2)	O1w–Co1–O2w	93.9(1)
		O1w–Co1–N1	90.4(1)
		O1w–Co1–N1	89.6(1)
Co3–O5w	2.086(1)	O5w–Co3–O5w	180.0(1)
Co3–O5w	2.086(1)	O5w–Co3–O6w	85.9(1)
Co3–O6w	2.106(1)	O5w–Co3–O6w	94.1(1)
Co3–O6w	2.106(1)	O5w–Co3–O7w	86.4(1)
Co3–O7w	2.105(1)	O5w–Co3–O7w	93.6(1)
Co3–O7w	2.105(1)	O5w–Co3–O6w	94.1(1)
		O5w–Co3–O6w	85.9(1)
		O5w–Co3–O7w	93.6(1)
		O5w–Co3–O7w	86.4(1)
		O6w–Co3–O6w	180.0(1)
		O6w–Co3–O7w	94.1(1)
		O6w–Co3–O7w	85.9(1)
		O6w–Co3–O7w	85.9(1)
		O7w–Co3–O6w	94.1(1)
		O7w–Co3–O7w	180.0(1)

TABLE III Hydrogen bond lengths (Å) and angles (°) for **1**

O1w–H11···O7	2.697(2)	171(2)	O3w–H31···O4	2.743(2)	158(2)
O1w–H12···O6	2.747(2)	168(2)	O3w–H32···O8	2.685(2)	178(2)
O2w–H21···O3	2.647(2)	175(2)	O4w–H41···O2	2.719(2)	167(2)
O2w–H22···O15w	3.040(2)	130(2)	O4w–H42···O4	2.710(2)	165(2)
O2w–H22···O6	3.103(2)	142(2)			
O5w–H51···O11w	2.686(2)	172(2)	O8w–H81···O14w	2.708(2)	174(2)
O5w–H52···N8	2.845(2)	165(2)	O8w–H82···N2	2.890(2)	166(2)
O6w–H61···N6	2.870(2)	167(2)	O9w–H91···N4	2.842(2)	169(2)
O6w–H62···O15w	2.710(2)	170(2)	O9w–H92···O12w	2.718(2)	168(2)
O7w–H71···N3	2.872(2)	170(2)	O10w–H101···N7	2.884(2)	165(2)
O7w–H72···O13w	2.711(2)	173(2)	O10w–H102···O16w	2.666(2)	174(2)
O11w–H111···O1	2.779(2)	169(2)	O11w–H112···O2	2.951(2)	165(2)
O12w–H121···O2	2.885(2)	162(2)	O12w–H122···O5	2.818(2)	159(2)
O13w–H131···O7	2.796(2)	173(2)	O13w–H132···O1	2.847(2)	174(2)
O14w–H141···O6	2.880(2)	164(2)	O14w–H142···O5	2.772(2)	177(2)
O15w–H151···O1	2.765(2)	174(2)	O15w–H152···O8	2.724(2)	171(2)
O16w–H161···O3	2.772(2)	167(2)	O16w–H162···O5	2.880(2)	173(3)

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RESULTS AND DISCUSSION

Structure of $\{[Co(hmt)_2(H_2O)_4][Co(H_2O)_6]\}(SO_4)_2 \cdot 6H_2O$, 1

Compound **1** consists of two different cobalt(II) complex cations, sulfate anions and lattice water molecules. Its crystal structure shows two symmetry-independent $[Co(hmt)_2(H_2O)_4]^{2+}$ cations and two symmetry-independent $[Co(H_2O)_6]^{2+}$ cations

(both of $\bar{1}$ point symmetry). The cobalt atoms of both cations have distorted octahedral coordination geometry. Each $[Co(hmt)_2(H_2O)_4]^{2+}$ (Fig. 1; the similar figure for the Co2 complex is not shown) cation exhibits pseudo Jahn–Teller distortion with two long axial Co–N bonds (2.354, 2.355 Å) and four short Co–O bonds (2.046–2.072 Å). This distortion is not Jahn–Teller tetragonal elongation because the mean μ_{eff} value 3.63 BM for the Co atom in **1** is only consistent with the Co atom having a $t_{2g}^5 e_g^2$ electronic configuration with three unpaired electrons. By contrast, the octahedral geometry of each $[Co(H_2O)_6]^{2+}$ cation (Fig. 2; similarly, that for Co4 is not shown) shows normal slight distortion [2], and the four equatorial bonds are distinctly longer than the two axial bonds (Table II). Unlike the bulkier axial hmt molecules in $[Co(hmt)_2(H_2O)_4]^{2+}$, the smaller axial water molecules in $[Co(H_2O)_6]^{2+}$ can approach nearer to the Co atom.

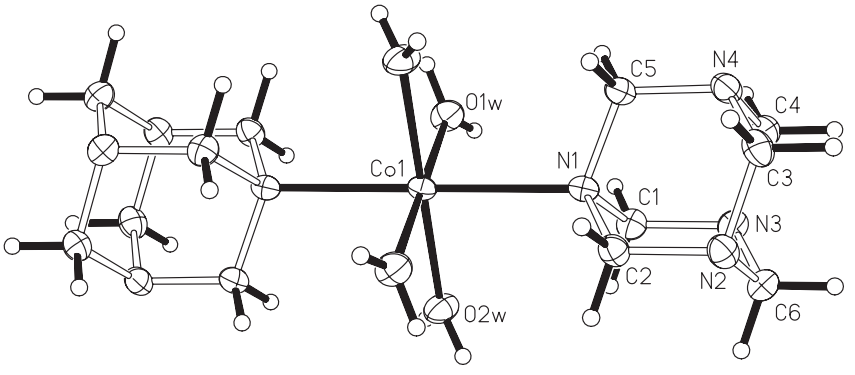

FIGURE 1 ORTEP plot of $[Co(hmt)_2(H_2O)_4]^{2+}$ with atom numbering scheme. The displacement ellipsoids are drawn at 40% probability.

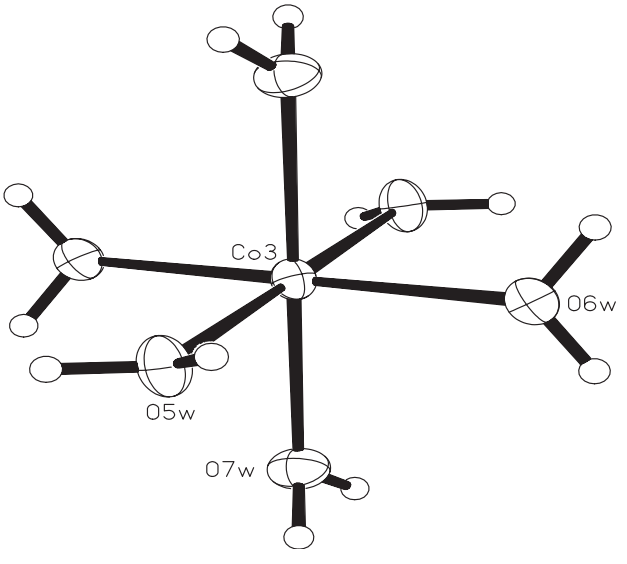

FIGURE 2 ORTEP plot of $[Co(H_2O)_6]^{2+}$ with atom numbering scheme. The displacement ellipsoids are drawn at 40% probability.

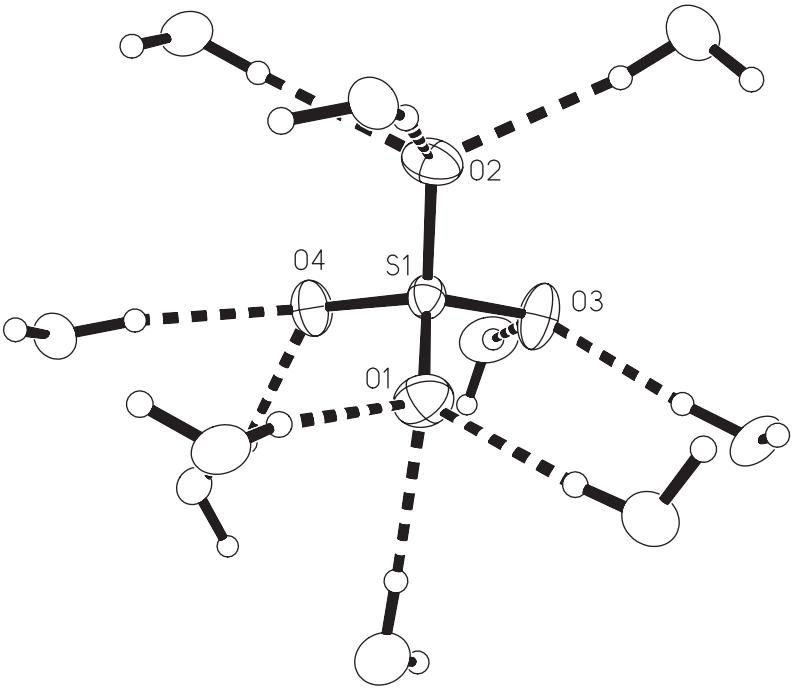

FIGURE 3 ORTEP plot of SO_4^{2-} and its hydrogen bonding to 10 water molecules.

Extensive hydrogen bonds bind and assemble the above cobalt(II) cations, sulfate anions and lattice water molecules. The two types of cations are linked to the sulfate anions via the coordinated and lattice water molecules in the crystal structure. The sulfate anion is hydrogen bonded to ten water molecules. Two types of sulfate oxygen atoms are distinguished: one oxygen atom is hydrogen bonded to two water molecules and the other is hydrogen bonded to three water molecules (Fig. 3). Interaction exists between $[Co(hmt)_2(H_2O)_6]^{2+}$ cations and $[Co(H_2O)_6]^{2+}$ cations via the coordinated hmt molecules. Here, three uncoordinated hmt nitrogen atoms of $[Co(hmt)_2(H_2O)_6]^{2+}$ are each hydrogen bonded to a coordinated water molecule of adjacent $[Co(H_2O)_6]^{2+}$ cations. Uniquely, one of the coordinated water molecules (O2w) exhibits a higher number of hydrogen bonds; one of its hydrogen atoms is hydrogen bonded to O15w (lattice water) and O6 (sulfate). In addition, the lattice water molecules are hydrogen bonded to sulfate anions and coordinated water molecules; each lattice water molecule has three hydrogen bonds. Thus, extensive hydrogen bonding assembles the cations, anions and lattice water molecules into a three-dimensional network.

Infrared Spectral Analysis of 1 and 2

The infrared spectra of **1** (Fig. 4), **2** and hmt were recorded in the range 4000–600 cm^{-1} as KBr disks and their absorption peaks/bands are listed in Table IV. The presence of lattice water and coordinated water molecules in **1**, as shown in the crystal structure, can also be distinguished by infrared spectral studies [14,15]. The broad band at 3229.4 cm^{-1} and a sharp peak at 1620.9 cm^{-1} are attributed to ν(OH) and δ(HOH)

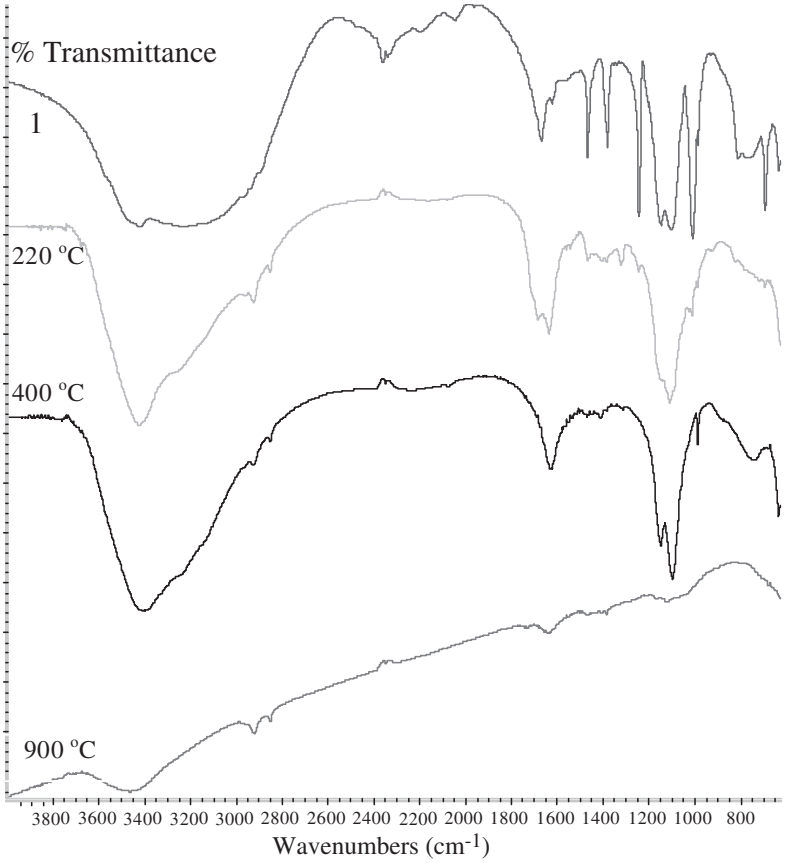

FIGURE 4 Infrared spectra of **1** and the residues at 220, 400 and 900°C.

TABLE IV Observed infrared frequencies and band assignments for **1**, **2** and hmt (cm^{-1})

1	**2**	*hmt*		*Band assignments*
		Ref. 3	*This work*	
3418.6	3421.0	–	–	OH stretch (coord. water)
3229.4	3233.4	–	–	OH stretch (lattice water)
1620.9	–	–	–	HOH bend (lattice water)
1465.3	1465.9	1489, 1456	1457.2	CH_2 scissors (hmt)
1380.5	1380.3	1370	1370.2	CH_2 wag (hmt)
1241.8	1242.2	1240	1237.5	CH_2 rock (hmt)
–	1144.8	–	–	
1008.2	1008.3	1007	1005.6	N–C stretch (hmt)
808.5	813.4	812	811.5	N–C stretch (hmt)
–	766.6	–	–	
690.2	690.2	690	671.9	N–C–N bend (hmt)
1668.1	1670.1	–	–	
1099.5	1103.3	–	–	S–O stretch
631.5	632.6	–	–	S–O stretch

of lattice water molecules while the higher energy peak at 3418.6 cm^{-1} is due to ν(OH) of the coordinated water molecule.

By comparison of our infrared spectrum of hmt and a recent detailed analysis and vibrational assignment of hmt [16], the spectral peaks and vibrational modes due to coordinated hmt in **1** have been identified. This is further correlated by infrared spectral studies of the residues of the thermal decomposition of **1**. The residue at 400°C shows the absence of these frequencies as all hmt molecules in **1** have decomposed and a hydrated cobalt sulfate is left as the residue. In addition, thermal analysis of pure hmt shows a decomposition temperature range of *ca* 96–244°C.

Unlike the sulfate ligand, the free sulfate ion has only two infrared-active vibrations at 1104 and 613 cm^{-1} [15]. By comparing with the infrared spectrum of cobalt(II) sulfate hydrate, the peaks at 1099.5 and 631.5 cm^{-1} can be assigned to S–O stretching vibrations in the sulfate ion of Compound **1**. The medium intensity absorption band of **1** at 1668.1 cm^{-1} is not identified; a similar band at 1654.2 cm^{-1} is present in the infrared spectrum of a known cobalt(II) sulfate hydrate.

As the infrared spectrum of **2** closely resembles that of **1**, Compound **2** is postulated to be similarly constituted and have a similar structure. Compound **2** is thus formulated as $\{[Ni(hmt)_2(H_2O)_4][Ni(H_2O)_6]\}(SO_4)_2 \cdot 6H_2O$. Based on the preceding analysis of **1**, the infrared spectral peaks of the Ni(II) analogue, **2**, have been assigned and are listed in Table IV. This proposed structure is further supported by the average magnetic moment of **2** (2.33 BM), which is consistent with nickel(II) having an octahedral coordination environment and $t_{2g}^6 e_g^2$ configuration with two unpaired electrons.

Thermal Decomposition of 1 and 2

The TG-DTA curves of **1** over the range 50–900°C show three decomposition steps at 100.6, 228.3 and 511.5°C (Table V). The residues at 220, 400 and 900°C together with their infrared spectra (Fig. 4) were analyzed. The first decomposition corresponds to loss of eight water molecules and one hmt molecule. The infrared spectrum of this purple-colored first residue, obtained on heating up to 220°C, shows the presence of hmt peaks at 1464.4, 1384.1, 1008.9 and 689.3 cm^{-1}. The diminished intensity of these peaks, compared to the corresponding peaks of **1**, suggests partial loss of hmt, which is a weakly bonded monodentate ligand (bond length 2.354–2.344 Å). Thermal analysis of pure hmt shows that hmt starts to decompose at 96°C. Thus, the loss in

TABLE V Thermal decomposition data for **1** and **2**

Decomposition temp. (°C) (% wt. loss)	*Theoretical loss* (%) (*molecules expelled*)	*Residue* (%)
Compound **1**		
100.6 (31.6)	32 (1 hmt + 8 H_2O)	68.4
228.3 (20.6)	20 (1 hmt + 2 H_2O)	47.8
511.5 (28.1)	28 (2 SO_3 + 5 H_2O)	19.9
Compound **2**		
78.2 (4.60)	4 (2 H_2O)	95.4
106.9 (26.1)	26 (1 hmt + 5 H_2O)	69.3
257.1 (22.0)	22 (1 hmt + 3 H_2O)	47.3
408.2 (10.1)	10 (5 H_2O)	37.2
488.8 (18.7)	18 (2 SO_3)	18.5

weight due to hmt may be ascribed to accumulated decomposition of hmt molecules in the solid of **1**.

The second decomposition peak at 228.3°C results from complete decomposition of hmt and further dehydration (two water molecules per unit of **1**). The infrared spectrum of the brown residue at 400°C shows absence of absorption peaks attributed to hmt. This complete loss of hmt from **1** is consistent with the analysis of the TG-DTA curves of pure hmt, which shows only one decomposition step at 244.4°C (100% loss over the temperature range *ca* 90–260°C). This means that the residue formed after the second decomposition step at 228.3°C is hydrated cobalt(II) sulfate with six water molecules. The infrared peaks at 1144.2, 1094.9 and 630.1 cm^{-1} of the residue at 400°C are attributed to S–O stretching frequencies while the bands at 3405.9 and 1625.9 cm^{-1} are due to water molecules. Thus, the complete loss or decomposition of the hmt in **1** is spread over two steps (1–1 at 100.6 and 228.3°C). This contrasts with the thermal decomposition of $[Co(NCS)(hmt)_2(H_2O)_2][Co(NCS)_2(H_2O)_4]\cdot H_2O$, where the similarly coordinated hmt (acting as monodentate) only decomposes between 200 and 500°C [14]. No evidence was provided for decomposition of the coordinated NCS ligand in the third decomposition step at 190°C and the presence of hmt in the subsequent residue. Another recent report [17] claimed the greater stability of both the uncoordinated protonated hmt and bridging hmt molecules in the thermal decomposition of $[Hhmt]_2[Zn_2(hmt)(NCS)_6]$, in which no decomposition occurs below 231°C. This apparent conflicting decomposition temperature/relative thermal stability of hmt in the present compounds and others may be due to changes in the hydrogen-bonding network and other structural properties.

The final decomposition step for **1** at 511.5°C involves further dehydration and decomposition of the sulfate. The almost complete dehydration of **1** is multistep (8–2–5 at 100.6, 228.3 and 511.5°C) and thus comparable to those found for $CoSO_4\cdot 7H_2O$ (1–3–2–1 at 119.6, 161.7, 184.7 and 294.5°C) and $CoSO_4\cdot 6H_2O$ (1–2–2–1 at 108.8, 161.7, 187 and 301.6°C) [18]. At 900°C, the last water molecule in **1** does not seem to be dehydrated. The first dehydration seems to involve expulsion of eight coordinated water molecules, each of which has two hydrogen bonds; the lattice water molecules are harder to remove because of the additional hydrogen bond. This is similar to dehydration of $[Co(NCS)(hmt)_2(H_2O)_2][Co(NCS)_2(H_2O)_4]\cdot H_2O$, where each of the four water molecules (coordinated) expelled (at 115°C) has only one hydrogen bond, and where each of the final three water molecules expelled (at 147°C) has two hydrogen bonds [14]. In both cases, the lower number of hydrogen bonds has resulted in easier thermal dehydration of coordinated water molecules compared to that of lattice water molecules.

The above decomposition of the sulfate is confirmed by the absence of S–O stretching frequencies in the infrared spectrum of the residue of **1** at 900°C. Thermal decomposition of anhydrous cobalt sulfate and other metal sulfates occurs at *ca* 550°C to yield sulfur trioxide gas and the corresponding metal oxides [19]. The final residue in the decomposition of **1** is postulated to have the empirical formula $Co_2O_3\cdot H_2O$, which has a formula weight corresponding to about 20.9% of **1**. The experimental percentage weight of the final residue is 19.9% and this substantiates the proposed formula of the final oxide formed.

As the infrared spectrum of **2** closely resembles that of **1**, it is reasonable to propose that the thermal decomposition of $\{[Ni(hmt)_2(H_2O)_4][Ni(H_2O)_6]\}(SO_4)_2\cdot 6H_2O$ (**2**) is similar to that of **1** (Table V). This is supported by the fact that the theoretical loss

in weight agrees well with the actual loss in weight in each decomposition step. The first decomposition step is due to loss of two water molecules at 78.2°C. This is followed by a second step due to expulsion of one hmt molecule together with five water molecules at 106.9°C. The third step involves loss of another hmt molecule together with three water molecules at 257.1°C. The subsequent steps include further dehydration (loss of five water molecules) at 408.2°C and decomposition of the sulfate at 488.8°C.

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