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Coordination-Driven Self-Assembly of a Novel Carbonato-Bridged Heteromolecular Neutral Nickel(II) Triangle by Atmospheric CO_2 Fixation

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Formation of a quasi-symmetrical μ_3-carbonato-bridged self-assembled heteromolecular triangle of Ni(II), $[(\mu_3\text{-}CO_3)\{Ni_2(salmeNH)_2(NCS)_2\}\{Ni(salmeNH_2)_2\}]\cdot Et_2O\cdot H_2O$ (HsalmeNH = 2-[(3-methylamino-propylimino)-methyl]-phenol) involves atmospheric CO_2 uptake in a neutral medium, by spontaneous self-reorganization of the starting mononuclear Ni(II)−Schiff-base complex, $[Ni(salmeNH)_2]$. The environment around Ni(II) in two of the subunits is different from the third one. The starting complex, $[Ni(salmeNH)_2]$, and one of the possible intermediate species, $[Ni(salmeNH_2)_2(NCS)_2]$, which has a very similar coordination environment to that in the third Ni(II) center, have been characterized structurally. A plausible mechanism for the formation of such a triangle has also been proposed. The compound shows a very strong antiferromagnetic coupling. Fit as a regular triangular arrangement gave $J = -53.1$, $g = 2.24$, and $R = 1.5 \times 10^{-4}$.

Introduction

The transition-metal-directed self-assembly of macrocycles and cage compounds has received considerable attention lately, leading to more and more complex architectures,[1] for example, squares and rectangles,[2–4] pentagons and hexagons,[5] catenanes, nanotubes and polytubes,[6] bowls and cages,[7] cuboctahedra, and dodecahedra,[8] among many others. There have been many concepts and ideas to predict which species will self-assemble in solution,[1,9] and these consid-

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erations are mainly based on the information stored in the building blocks, that is, the number of donor groups, their positioning in space, the electronic configuration of the metal ions, and the specificity of molecular recognition. In contrast to this variety of structures, one of the simplest possible two-dimensional figures—the triangle—has proven to be relatively rare.[10] Although the use of a wide variety of transition metal ions diversifies this field of supramolecular chemistry considerably,[1,11] most of the triangular molecules reported so far consist of Pt(II) or Pd(II).[1b,3b,c,5a,10b] A completely new variety of molecular triangle, based on atmospheric CO_2 fixation mostly by cadmium(II)[12] complexes, has also been observed by many other scientists. Recently, carbonate incorporated triangular arrangement of lanthanides has been reported as a part of a more complex structure.[13] In this class of complexes, each of the three oxygen atoms of a carbonate ion acts as an approximately 180° donor unit, and the metal acts as a 60° acceptor.

Indeed, chemical fixation and activation of carbon dioxide by metal complexes has drawn long-standing interest as the fundamental understanding, and the application of the reaction may lead to some practical means of eliminating the CO_2 present in air, and also because CO_2 could be used as an attractive C_1 feedstock for the preparation of useful carbon-containing compounds by the reaction of CO_2 with metal complexes.[14] Moreover, the carbonate anion can act as an extremely versatile bridging ligand, due to its flexibility in coordination modes. It also shows a wide variety of magnetic behavior ranging from moderate or weak ferromagnetism to very strong antiferromagnetic coupling, which results in full coupling at room temperature (diamagnetism) in some cases.[15] However, the magnetic properties of some coordination modes of carbonate still remain unexplored.

Herein, we report a novel μ_3-carbonato bridged self-assembled heteromolecular triangle consisting of two different types of molecular species based on $Ni(NCS)_2$ and a Schiff base (HsalmeNH = 2-[(3-methylamino-propylimino)-methyl]-phenol)), the 1:1 condensate of salicyldehyde and N-methyl-1,3-propanediamine. An overwhelming majority of self-assembled polynuclear complexes exhibits symmetry. Metal coordination hetero assemblies have been little reported because of the difficulty in controlling the simultaneous formation of several species. This compound shows several remarkable features: (i) it is not only the first supramolecular triangle consisting of Ni(II) but, to our knowledge, the first heteromolecular triangle with any other metal ion in which two different types of molecules are self-assembled; (ii) it shows that exclusive formation of metal coordination hetero assemblies can be achieved, with the help of additional H-bonding interactions; (iii) it is formed by the self-selection of autogenerated species under the reaction conditions—a phenomenon which is extremely important in the creation of complex molecules with specific activity in the evolution of life processes; (iv) it is the first compound which shows the very rare bis-tridentate μ_3-coordination mode for the carbonate ion in nickel(II) and hence provides the first opportunity to evaluate the magnetic interactions between the Ni(II) centers through such a mode.

Experimental Section

Materials. The reagents and solvents used were of commercially available reagent quality, unless otherwise stated.

Synthesis of the Schiff-Base Ligand 2-[(3-Methylamino-propylimino)-methyl]-phenol (HsalmeNH). The Schiff base was prepared by the condensation of salicylaldehyde (1.05 mL, 10 mmol) and N-methyl-1,3-propanediamine (1.04 mL, 10 mmol) in methanol (10 mL), as reported previously.[16]

Synthesis of $[Ni(salmeNH)_2]$ (1). $Ni(NCS)_2\cdot 4H_2O$ (1.237 g, 5 mmol), dissolved in 10 mL of hot methanol, was added to a methanolic solution (10 mL) of the ligand (HsalmeNH; 10 mmol). Triethylamine (1.4 mL, 10 mmol) was added dropwise to this solution with constant stirring. The color of the solution turned to light green. The filtrate was left to stand overnight in the air, when straw-yellow-colored X-ray-quality single crystals of complex **1** appeared at the bottom of the vessel upon slow evaporation of the solvent. Yield: 1.76 g; 80%. Anal. calcd for $C_{22}H_{30}N_4NiO_2$: C, 59.89; H, 6.85; N, 12.70. Found: C, 59.72; H, 6.79; N, 12.75. IR (KBr pellet, cm^{-1}): 3330 ν(NH), 1636 ν(C=N). λ_{max} (solid, reflectance): 569, 928 nm. Magnetic moment = 3.08 μ_B.

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Table 1. Crystal Data and Structure Refinement of Complexes **1**−**3**

	1	**2**	**3**
empirical formula	$C_{22}H_{30}N_4NiO_2$	$C_{24}H_{32}N_6NiO_2S_2$	$C_{51}H_{72}N_{10}Ni_3O_9S_2$
fw	441.19	559.39	1209.44
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
cryst syst	monoclinic	monoclinic	monoclinic
a/Å	6.8166(4)	11.9536(15)	21.5515(5)
b/Å	8.7263(10)	7.4582(8)	12.0674(3)
c/Å	17.778(2)	14.9241(8)	23.3045(5)
β/deg	96.099(8)	97.414(7)	106.543(2)
V/Å^3	1051.5(2)	1319.4(2)	5809.9(2)
Z, calculated density	2, 1.393 g/cm^3	2, 1.408 g/cm^3	4, 1.380 g/cm^3
abs coeff (μ) mm^{-1}	0.948 (Mo Kα)	0.927 (Mo Kα)	1.094 (Mo Kα)
F(000)	468	588	2536
cryst size	0.03 × 0.03 × 0.27	0.05 × 0.05 × 0.30	0.03 × 0.04 × 0.21
refinement method	SHELXL-97 on F^2	SHELXL-97 on F^2	SHELXL-97 on F^2
θ range for data collection	2.30−30.00°	2.34−30.00°	2.27−30.00°
R(int)	0.038	0.123	0.073
no. of unique data	2753	3810	16814
no. of data with $I > 2\sigma(I)$	1593	2298	9240
R1, wR2	0.0320, 0.0745	0.1130, 0.3746	0.0811, 0.1954
goodness of fit on F^2	0.747	1.065	1.031
largest diff. peak and hole	0.279, 0.342	2.594, −1.700	1.375, −1.997

Synthesis of [Ni(salmeNH$_2$)$_2$(NCS)$_2$] (2). $Ni(NCS)_2 \cdot 4H_2O$ (1.237 g, 5 mmol), dissolved in 10 mL of hot methanol, was added to a methanolic solution (10 mL) of the ligand (HsalmeNH; 10 mmol) and stirred for ca. 10 min. The color of the solution turned to deep green. The solution was left to stand overnight in the air, when deep-green, X-ray-quality single crystals of complex **2** appeared at the bottom of the vessel upon slow evaporation of the solvent. Yield: 2.37 g; 85%. Anal. calcd for $C_{24}H_{32}N_6NiO_2S_2$: C, 51.53; H, 5.77; N, 15.02. Found: C, 51.42; H, 5.79; N, 14.95 IR (KBr pellet, cm^{-1}): 3072 (broad) $\nu(NH_2)$, 1630 ν(C═N), 2105 ν(SCN). λ_{max} (solid, reflectance): 577, 930 nm. Magnetic moment = 3.12 μ_B

Synthesis of [(μ_3-CO$_3$){Ni$_2$(salmeNH)$_2$(NCS)$_2$}{Ni(salmeNH$_2$)$_2$]·Et$_2$O·H$_2$O (3). A methanolic solution (5 mL) of $Ni(NCS)_2 \cdot 4H_2O$ (1.237 g, 5 mmol) was mixed with a methanolic solution (5 mL) of complex [Ni(salmeNH)$_2$] (4.390 g, 10 mmol) and stirred for ca. 10 min. Upon standing the mixture overnight in an open atmosphere, a green precipitate separated out. The green solid was then filtered and washed with diethyl ether and then redissolved in CH_3CN. Layering of the green solution with diethyl ether gave well-formed X-ray-quality bluish-green single crystals of **3**. The crystals were collected and dried in vacuo. Yield: 40%; 2.4 g. We are able to reproduce the same complex by passing CO_2 directly to the methanol solution containing complexes [Ni(salmeNH)$_2$] and $Ni(NCS)_2 \cdot 4H_2O$ in a 2:1 molar ratio, with higher yield and very high purity, as confirmed by C, H, and N analysis; the spectral studies; and the X-ray powder diffraction pattern (Yield: 60%; 3.6 g). Anal. calcd for $C_{51}H_{72}N_{10}Ni_3O_9S_2$: C, 50.65; H, 6.00; N, 11.58. Found: C, 50.72; H, 5.89; N, 11.45. IR (KBr pellet, cm^{-1}): 3205, 3030 (broad) $\nu(NH_2)$, 1628 ν(C═N), 3435 ν(OH), 2087 ν(NCS). λ_{max} (solid, reflectance): 570, 932 nm.

Physical Measurements. Elemental analyses (C, H, and N) were performed using a Perkin-Elmer 240C elemental analyzer. IR spectra in KBr (4500−500 cm^{-1}) were recorded using a Perkin-Elmer RXI FT-IR spectrophotometer. Electronic spectra in the solid state (1000−250 nm) were recorded with a Hitachi U-3501 spectrophotometer. The effective moments at room temperature for complexes **1** and **2** were evaluated from magnetic susceptibility measurement with an EG and G PAR 155 vibrating-sample magnetometer. The magnetic measurement for complex **3** was carried out in the "Servei de Magnetoquímica" (Universitat de Barcelona) on polycrystalline samples (20 mg) with a Quantum Design SQUID MPMSXL magnetometer in the temperature range of 2−300 K, and the magnetic field was 5000 G. The diamagnetic corrections were evaluated from Pascal's constants.

Crystal Data Collection and Refinement. Crystal data for the three crystals are given in Table 1. Intensity data were measured via the Oxford X-Calibur CCD System using Mo Kα radiation. The crystals were positioned at 50 mm from the CCD. A total of 321 frames were measured with a counting time of 10 s for **1** and **3** and of 40 s for **2** to give 2753, 3810, and 16 814 independent reflections for **1**, **2**, and **3**, respectively. Data analyses were carried out with the Crysalis program.[17] The structures were solved using direct methods with the Shelxs97 program.[18] The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Empirical absorption corrections were carried out using the ABSPACK program.[19] The structures were refined on F2 using Shelxl97[18] to give R1 = 0.0320, 0.1130, and 0.0811 and wR2 = 0.0665, 0.3372, and 0.1669 for 1593, 2298, and 9240 independent reflections, respectively, with $I > 2\sigma(I)$ for **1**, **2**, and **3**, respectively.

Results and Discussion

Synthesis of the Complexes. The addition of a methanol solution of $Ni(SCN)_2$ to a methanol solution of the ligand (HsalmeNH) followed by triethylamine results in a straw-yellow-colored crystalline compound of [Ni(salmeNH)$_2$] (**1**). A neutral methanol solution of complex **1** and $Ni(NCS)_2 \cdot 4H_2O$ (in a 2:1 molar ratio) uptakes CO_2 from the atmosphere and yields the carbonato-bridged trinuclear species, **3**. One of the interesting features of complex **3** is that it consists of two different types of molecules. We have observed earlier that the reaction of $[Ni(L)_2]^n$ (where L = tridentate Schif base and $n = 0$ or $+2$) with $Ni(NCS)_2 \cdot 4H_2O$ yielded readily the mono-Schiff base complex NiLNCS.[20] Therefore, the two identical molecular parts containing the Ni(salmeNH)(NCS)

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(17) *Crysalis*, version 1; Oxford Diffraction Ltd.: Oxford, U.K., 2005.

(18) G. M. Sheldrick, *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.

(19) *ABSPACK*; Oxford Diffraction Ltd; Oxford, U.K., 2005.

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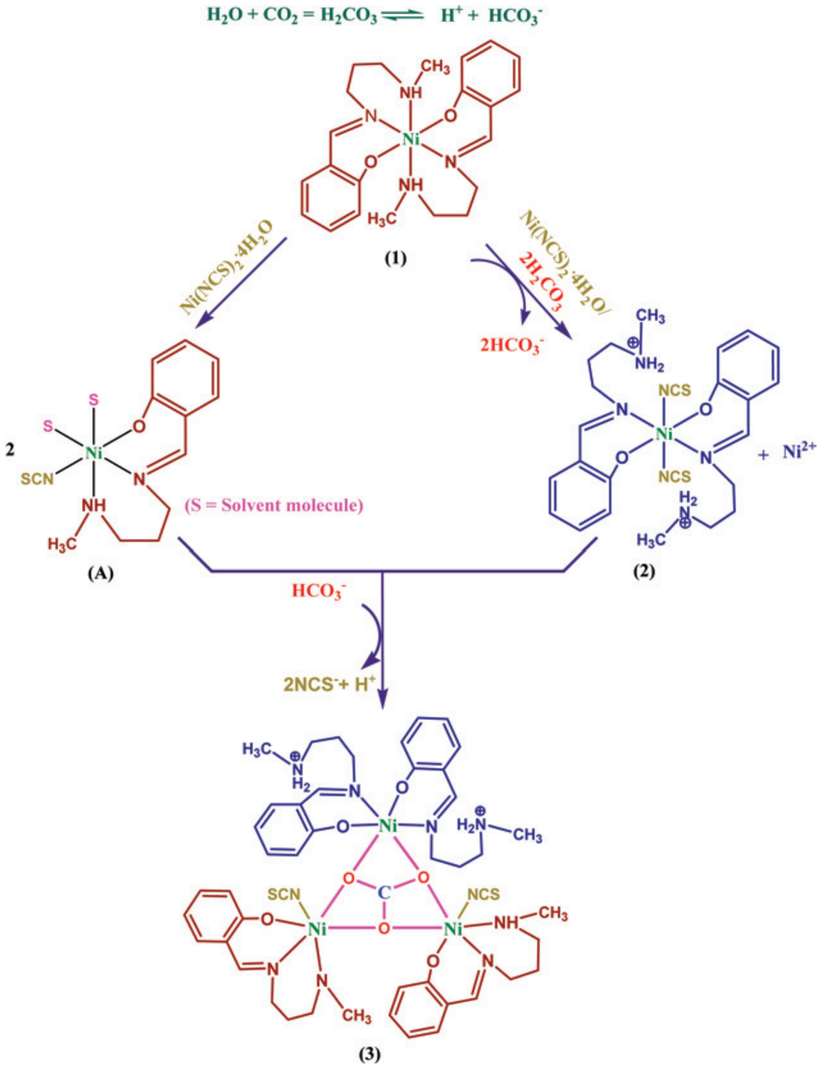
Scheme 1



(**A**) fragment (Scheme 1) are expected to be produced by the reaction of $Ni(SCN)_2$ and $[Ni(salmeNH)_2]$. However, the other part that consists of the $Ni(salmeNH_2)_2$ fragment, at first sight, seems to be a stranger, but its formation can be rationalized as follows: the atmospheric CO_2 upon getting dissolved into the reaction mixture forms carbonic acid, which seems to react with $[Ni(salmeNH)_2]$ (**1**) in the presence of thiocyanate ions to form the protonated Schiff base complex $[Ni(salmeNH_2)_2(NCS)_2]$ (**2**) and hydrogen carbonate ions. The trinuclear species, **3**, is generated subsequently by the reaction of 2**A** + **2** + HCO_3^{2-}, as shown in Scheme 1, by self-recognition of the intermediate species through coordination bonds and H bonds. In this context, it is worth mentioning that compound **3** is formed by the absorption of CO_2 in a neutral medium, unlike in most of the other reported systems where atmospheric CO_2 uptake takes place in alkaline solution. The driving force of CO_2 absorption in the neutral medium seems to be the ability of the Schiff base ligand in this reaction condition to act as a base. The tendency of the secondary amine group of the Schiff base to be protonated under slightly acidic conditions is proved categorically by the reaction of a methanol solution of Hsalme with $Ni(NCS)_2$, in the absence of any base, when the compound, $[Ni(salmeNH_2)_2(NCS)_2]$ (**2**), with a protonated and uncoordinated secondary amine group was formed. The isolation of **2** supports positively the proposed mechanism for the formation of the trinuclear complex as shown in Scheme 1. Both the precursor, $[Ni(salmeNH)_2]$ (**1**), and the probable intermediate, $[Ni(salmeNH_2)_2(NCS)_2]$ (**2**), have been characterized by crystal structure determination. Besides elemental analysis, all three complexes were initially characterized by IR and UV−vis spectra and room temperature magnetic susceptibility measurements.

IR and UV−vis Spectra and Magnetic Moment of the Complexes. In the IR spectra of complex **1**, the NH stretching mode is seen at 3330 cm^{-1} as a sharp band. A strong and sharp band due to azomethine ν(C═N) appears at 1636 cm^{-1}. In complex **2**, the asymmetric and symmetric stretching vibrations for the protonated secondary amine group appear together as a broad band at 3072 cm^{-1}. The appearance of the NH_2 band at a comparatively lower frequency is probably due to the involvement in hydrogen bonding of both amine hydrogens. A strong absorption band at 2105 cm^{-1} corroborates the presence of a N-bonded

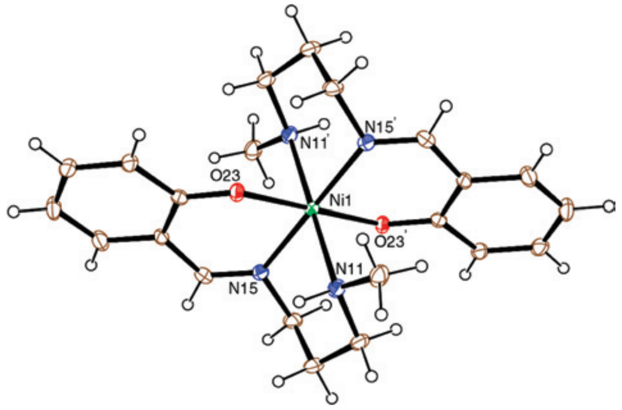


Figure 1. ORTEP-3 view of the asymmetric unit of **1** with ellipsoids at 25% probability. The metal is situated on a crystallographic center of symmetry. Atoms marked with a prime are transformed by symmetry element $1 - x$, $1 - y$, $1 - z$.

thiocyanate group in the complex.[20b,21] The band due to azomethine ν(C=N) appears at 1630 cm^{-1}. In complex **3**, the stretching modes of the secondary amine group are observed at 3205 cm^{-1} as a sharp band and at 3030 cm^{-1} as a broad band. The lower-energy band seems to be due to the H-bonded protonated amine groups. The appearance of a broad band near 3435 cm^{-1} indicates the presence of a water molecule. The band due to azomethine ν(C=N) appears at 1628 cm^{-1}. The presence of a N-bonded thiocyanate group in the complex is indicated by the appearance of a strong absorption band at 2087 cm^{-1}.[20b,21]

The solid-state reflectance spectra of all of the complexes are recorded. In all three complexes, a broad band near 930 nm, well-separated from the second transition near 570 nm, is observed, as is usual for octahedral Ni(II). The higher-energy d−d bands are obscured by strong charge-transfer transitions. Room temperature magnetic susceptibility measurements show that both complexes **1** and **2** have magnetic moments close to 3.1 μ_B, as expected for discrete magnetically noncoupled octahedral nickel(II) ion.

Description of the Structure of [Ni(salmeNH)$_2$] (1). The structure of **1** contains a discrete centrosymmetric molecule of [Ni(salmeNH)$_2$], as shown in Figure 1 together with the numbering scheme in the metal coordination sphere. The selected bond lengths and angles are summarized in Table 2. The metal atoms are in six-coordinate octahedral environments, being bonded to the two tridentate ligands, which occupy the facial positions. The ligand encapsulates the divalent metal ion through two amine nitrogen (N11 and N11′), two imine nitrogen (N15 and N15′), and two phenoxo oxygen atoms (O23 and O23′) of the Schiff base moiety. Phenoxo oxygen (O23 and O23′) and imine nitrogen (N15 and N15′) atoms of the ligands constitutes the basal plane. There is no deviatation of the Ni atom from the basal plane as imposed by the symmetry. The unique bond lengths are Ni(1)−N(11) = 2.170(2), Ni(1)−N(15) = 2.053(2), and Ni(1)−O(23) = 2.033(1) Å. The two axial positions are occupied by amine nitrogen atoms (N11 and N11′) of the ligand. The six-membered ring comprising the nickel, imine N atoms, three propylene C atoms, and an amino N atom adopts a chair conformation, and that containing nickel, imine N atoms, three benzylic C atoms, and a phenoxo O atom adopts a screw-boat conformation (the intermediate angle between the two planes consisting of salicylidene and amine is 88.67°).

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Complex **1**[a]

Ni1−O23	2.0330(13)	O23−Ni1−N11	88.23(6)
Ni1−N11	2.1701(17)	O23−Ni1−N15	86.76(5)
Ni1−N15	2.0532(14)	O23−Ni1−O23′	180.00
Ni1−O23′	2.0330(13)	O23−Ni1−N11′	91.77(6)
Ni1−N11′	2.1701(17)	O23−Ni1−N15′	93.24(5)
Ni1−N15′	2.0532(14)	N11−Ni1−N15	82.31(6)
		O23′−Ni1−N11	91.77(6)
		N11−Ni1−N11′	180.00
		N11−Ni1−N15′	97.69(6)
		O23′−Ni1−N15	93.24(5)
		N11′−Ni1−N15	97.69(6)
		N15−Ni1−N15′	180.00
		O23′−Ni1−N11′	88.23(6)
		O23′−Ni1−N15′	86.76(5)
		N11′−Ni1−N15′	82.31(6)

[a] Symmetry code: $' = 1 - x, 1 - y, 1 - z$.

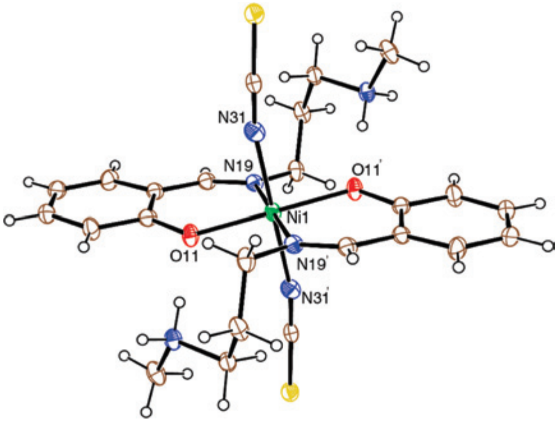


Figure 2. ORTEP-3 view of the asymmetric unit of **2** with ellipsoids at 25% probability. The metal atom occupies a crystallographic center of symmetry. Atoms marked with a prime are transformed by symmetry element $1 - x$, $1 - y$, $1 - z$.

Description of the Structure of [Ni(salmeNH$_2$)$_2$(NCS)$_2$] (2). The structure of **2** consists of discrete centrosymmetric molecules of Ni(salmeNH$_2$)$_2$(NCS)$_2$, as shown in Figure 2 together with the numbering scheme in the metal coordination sphere. The selected bond lengths and angles are summarized in Table 3. The metal atom has a slightly distorted six-coordinate octahedral environment. The phenoxo oxygen atoms (O11 and O11′) and imine nitrogen atoms (N19 and N19′) of the two Schiff base ligands constitute the equatorial plane. The two axial positions are occupied by nitrogen (N31 and N31′) atoms of the thiocyanate group. The six-membered chelate rings incorporating the salicylidene core are essentially planar with no atoms deviating more than 0.13 Å from the mean planes passing through them. One interesting feature of this complex is that the Schiff base, which is potentially tridentate, acts as a bidentate ligand coordinating only through O(11) and N(19). The third possible donor atom, N(23), is protonated, which

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(21) (a) Mukherjee, A. K.; Mukherjee, M.; Welch, A. J.; Ghosh, A.; De, G.; Ray Chaudhuri, N. *J. Chem. Soc., Dalton Trans.* **1987**, 997–1000. (b) Mukherjee, P.; Biswas, C.; Drew, M. G. B.; Ghosh, A. *Polyhedron* **2007**, *26*, 3121–3128.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for Complex **2**[a]

Ni1−O11	2.012(6)	O11−Ni1−N19	88.9(2)
Ni1−N19	2.095(6)	O11−Ni1−N31	89.8(3)
Ni1−N31	2.091(7)	O11−Ni1−O11′	180.00
Ni1−O11′	2.012(6)	O11−Ni1−N19′	91.1(2)
Ni1−N19′	2.095(6)	O11−Ni1−N31′	90.2(3)
Ni1−N31′	2.091(7)	N19−Ni1−N31	92.4(3)
		O11′− Ni1−N19	91.1(2)
		N19−Ni1−N19′	180.00
		N19−Ni1−N31′	87.6(3)
		O11′−Ni1−N31	90.2(3)
		N19′−Ni1−N31	87.6(3)
		N31−Ni1−N31′	180.00
		O11′−Ni1−N19′	88.9(2)
		O11′−Ni1−N31′	89.8(3)
		N19′−Ni1−N31′	92.4(3)

[a] Symmetry code: ′ = 1 − *x*, 1 − *y*, 1 − *z*.

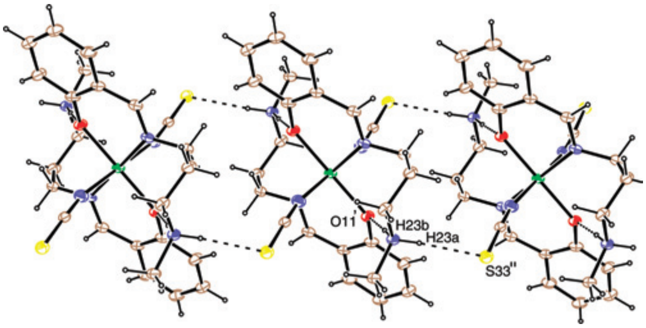

Figure 3. Hydrogen-bonded 1D chain of complex **2**. The intermolecular hydrogen bonds are shown as dashed lines; atoms marked with a (′) and (″) are transformed by the symmetry elements 1 − *x*, 1 − *y*, 1 − *z* and *x*, 1 + *y*, *z*, respectively.

allows the charge on the complex to be balanced, and it is not bonded to the metal but forms a strong intramolecular hydrogen bond to O11′ (1 − *x*, 1 − *y*, 1 − *z*) at 2.595 Å with N(23)−H(23b)···O(11)′ 177° and H(23b)···O(11)′ 1.70 Å. The other amine hydrogen atom, H(23a), forms a relatively weak intermolecular hydrogen bond to S33″ at 3.224 Å with N(23)−H···S(33″) 167° and H···S(33)″ 2.31 Å to form an infinite 1-D hydrogen-bonded chain, as shown in Figure 3 (Table 4).

Description of the Structure of [(μ_3-CO_3){Ni_2(salmeNH)$_2$(NCS)$_2$}{Ni(salmeNH$_2$)$_2$]·Et_2O·H_2O (3). The crystal structure of **3** comprises of discrete trimeric units of the neutral compound [(μ_3-CO_3){Ni_2(salmeNH)$_2$(NCS)$_2$}{Ni(salmeNH$_2$)$_2$], together with one solvent molecule of diethylether and two water molecules with 50% occupancy. A labeled diagram is shown in Figure 4. In the trimeric structure, the three nickel atoms are bridged in a μ_3 fashion by a single carbonate ion *via* its oxygen atoms, showing a very rare bis-tridentate coordination mode of the carbonate anion. The three Ni−O−Ni angles are close to 180°; thus, Ni(1)−O(1)−Ni(2) = 176.8(2), Ni(1)−O(2)−Ni(3) = 175.9(2), and Ni(2)−O(3)−Ni(3) = 178.7(2)°, and the Ni−Ni bond distances are Ni(1)−Ni(2) = 4.386(1) Å, Ni(1)−Ni(3) = 4.409(1) Å, and Ni(2)−Ni(3) = 4.289(1) Å, forming an approximate equilateral triangle. The carbonato ligand together with three Ni centers is planar, showing the average O−C−O bond angle to be 119.7°. The C−O−Ni angles are close to 90°; thus, the oxygen atoms are three-coordinate with a T-shaped coordination sphere. Dimensions in the metal coordination spheres of complex **3** are given in Table 5.

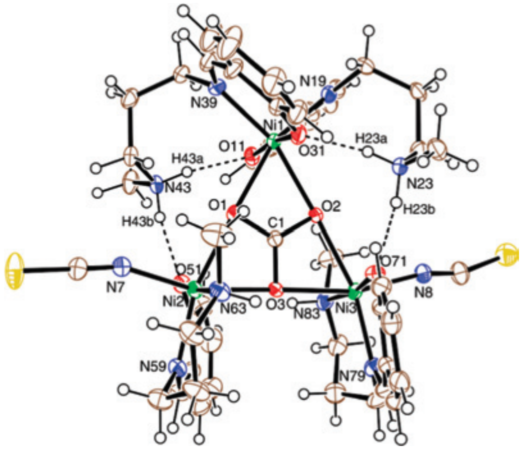

Figure 4. The structure of **3** with ellipsoids at 50% probability. H_2O and $(CH_3CH_2)_2O$ are omitted for clarity.

Table 4. Hydrogen-Bond Geometries in Compounds **2** and **3** (in Å and deg)[a]

D−H···A	*d*(D−H)	*d*(D···A)	*d*(H···A)	<(D−H···A)
		Compound **2**		
N23−H23a···S33″	0.9000	3.225(7)	2.3400	167.00
N23−H23b···O11′	0.9000	2.594(9)	1.7000	177.00
		Compound **3**		
N23−H23a···O31	0.9000	2.685(5)	1.8000	168.00
N23−H23b···O71	0.9000	2.714(5)	1.8200	169.00
N43−H43a···O11	0.9000	2.714(5)	1.8200	171.00
N43−H43b···O51	0.9000	2.734(6)	1.8500	166.00

[a] Symmetry code. ″ = (*x*, 1 + *y*, *z*), ′ = (1 − *x*, 1 − *y*, 1 − *z*).

The three nickel atoms are octahedrally coordinated, but the environments around the three Ni centers are not equivalent. Ni(2) and Ni(3) have similar coordination spheres, being bonded to the mononegative terdentate ligand (salmeNH), two oxygen atoms from the central carbonate anion, and a thiocyanate attached through nitrogen which is trans to the carbonate oxygen atom O(3) in both cases. These Ni(2)−O(3) and Ni(3)−O(3) bond lengths trans to thiocyanate at 2.144(3) and 2.145(3) Å are significantly shorter than the other bonds to the carbonate oxygen atoms, Ni(2)−O(1) being 2.202(3) and Ni(3)−O(2) being 2.208(3) Å, which are trans to the imino nitrogen atoms of the tridentate ligands (salmeNH). Bond lengths between the metal and the donor atoms of the tridentate ligand are as expected with bonds to the imino nitrogen atoms Ni(2)−N(59) and Ni(3)−N(79) being shorter at 2.035(4) and 2.030(4) Å than the bonds to the amine nitrogen atoms Ni(2)−N(63) and Ni(3)−N(83), 2.109(4) and 2.105(4) Å, respectively.

By contrast for Ni(1), there is no thiocyanate anion. Instead, the metal is attached to two neutral ligands (SalmeNH$_2$), but these are bidentate rather than tridentate, being bonded to N(11) and O(19) from one ligand and N(31) and O(39) from the second. In the two ligands, the amino nitrogen atoms N(23) and N(43) are protonated and not bonded to the metal as in **2**. Instead each amine hydrogen forms two very strong intramolecular hydrogen bonds to adjacent oxygen atoms of the Schiff base, as shown in Figure 4. The dimensions for the H···O and N···O distances and N−H···O angles for N(23) are 1.80 Å, 2.685(5) Å, and 168° to O(31)

Table 5. Dimensions (Distances, Å, Angles, deg) in the Metal Coordination Spheres of Complex **3**

Ni1		Ni2		Ni3	
Ni1−O1	2.185(4)	Ni(2)−N(7)	2.014(4)	Ni(3)−O(2)	2.208(3)
Ni1−O2	2.203(3)	Ni(2)−O(1)	2.202(3)	Ni(3)−O(3)	2.145(3)
Ni1−O11	1.999(3)	Ni(2)−O(3)	2.144(3)	Ni(3)−O(71)	2.019(3)
Ni1−O31	2.008(3)	Ni(2)−O(51)	2.022(3)	Ni(3)−O(79)	2.030(4)
Ni1−N19	2.042(4)	Ni(2)−N(59)	2.034(4)	Ni(3)−N(8)	2.028(4)
Ni1−N39	2.044(4)	Ni(2)−N(63)	2.109(4)	Ni(3)−N(83)	2.105(4)
O(11)−Ni(1)−O(31)	173.29(1)	N(7)−Ni(2)−O(51)	94.34(2)	O(71)−Ni(3)−N(8)	94.63(2)
O(11)−Ni(1)−N(19)	90.07(2)	N(7)−Ni(2)−N(59)	95.13(2)	O(71)−Ni(3)−N(79)	89.93(2)
O(31)−Ni(1)−N(19)	93.80(2)	O(51)−Ni(2)−N(59)	89.17(2)	N(8)−Ni(3)−N(79)	94.16(2)
O(11)−Ni(1)−N(39)	93.92(2)	N(7)−Ni(2)−N(63)	91.06(2)	O(71)−Ni(3)−N(83)	170.52(2)
O(31)−Ni(1)−N(39)	90.84(2)	O(51)−Ni(2)−N(63)	172.58(2)	N(8)−Ni(3)−N(83)	91.25(2)
N(19)−Ni(1)−N(39)	99.67(2)	N(59)−Ni(2)−N(63)	95.42(2)	N(79)−Ni(3)−N(83)	97.06(2)
O(11)−Ni(1)−O(1)	86.88(1)	N(7)−Ni(2)−O(3)	162.86(2)	O(71)−Ni(3)−O(3)	87.95(1)
O(31)−Ni(1)−O(1)	87.59(1)	O(51)−Ni(2)−O(3)	88.31(1)	N(8)−Ni(3)−O(3)	164.37(2)
N(19)−Ni(1)−O(1)	159.69(1)	N(59)−Ni(2)−O(3)	101.84(2)	N(79)−Ni(3)−O(3)	101.27(1)
N(39)−Ni(1)−O(1)	100.57(1)	N(63)−Ni(2)−(3)	84.99(2)	N(83)−Ni(3)−O(3)	84.42(1)
O(11)−Ni(1)−O(2)	87.52(1)	N(7)−Ni(2)−O(1)	101.96(2)	O(71)−Ni(3)−O(2)	82.79(1)
O(31)−Ni(1)−O(2)	86.48(1)	O(51)−Ni(2)−(1)	82.91(1)	N(8)−Ni(3)−O(2)	103.52(2)
N(19)−Ni(1)−O(2)	98.76(1)			N(79)−Ni(3)−O(2)	161.33(4)
N(39)−Ni(1)−O(2)	161.51(1)			N(83)−Ni(3)−O(2)	88.61(4)
O(1)−Ni(1)−O(2)	61.07(1)			O(3)−Ni(3)−O(2)	61.46(1)

and 1.82 Å, 2.714(5) Å, and 169° to O(71), while for N(43) the dimensions are 1.82 Å, 2.714(5) Å, and 171 ° to O(11) and 1.85 Å, 2.734(5) Å, and 166° to O(51). A significant difference in the H-bonded structures of **2** and **3** is that, in the former, only one amine hydrogen atom is involved in strong intramolecular H bonding with the coordinated phenoxo group, but in the latter, both of the amine hydrogen atoms form strong intramolecular hydrogen bonds. The core structure of **3** is remarkable in that three Ni units are joined by a carbonate group (CO_3) in a symmetrical and very rare bis-tridentate coordination mode. The strong H bonds between [Ni(salmeNH_2)$_2$(NCS)$_2$] and [Ni(salmeNH)(NCS)] units seem to stabilize the triangular arrangement of the supramolecule. It is interesting to note that a related carbonato-bridged Ni_3 species was reported,[15e] where the μ_3-CO_3 acts as a bis-bidentate ligand and the closed triangular arrangement cannot be achieved, probably due to steric crowding as well as strain produced by the unfavorable angles for both donor and acceptor units (ideally, the angle around the octahedral metal center should be 90° and the lone pairs on donor oxygen atoms of carbonate should directed at an angle between 109 and 120°). In the present compound, the ability of self-generation of different species (e.g., complexes **A** and **2**) in situ and their self-organization driven together by the coordination bonds and strong H bonds seem to be the driving force for the formation of a closed triangular arrangement overcoming steric crowding and angular strain.

Magnetic Properties. The magnetic behavior of complex **3** was investigated in the temperature range of 2−300 K, and the magnetic field was 5000 G. The temperature dependence of $\chi_M T$ for complex **3** is shown in Figure 5. The plot is characteristic of a strongly antiferromagnetically coupled equilateral-triangular topology with local $S = 1$. At 300 K, the $\chi_M T$ value is approximately equal to 2.66 cm^3 mol^{-1} K, which is smaller than the expected value for three Ni(II) ions with $S = 1$. The $\chi_M T$ values continuously decrease from room temperature and reach a value of 0.37 cm^3 mol^{-1} K at 20 K. From 20 K, the slope of the curve changes and decreases smoothly, reaching a value of 0.17 cm^3 mol^{-1} K at 2 K.The geometrical parameters of the trinuclear Ni_3 entity correspond to a nearly equilateral triangular array of local $S = 1$ (Figure 6). We have fitted the experimental data, taking into account three, two, and one average J value. The best agreement was achieved in the temperature range 20−300 K and considering the exchange interactions between the three Ni(II) ions being equal, $J_1 = J_2 = J_3$. For this approximation, the system can be described by the following spin Hamiltonian:

$$H = -J(S_1S_2 + S_2S_3 + S_3S_1) \tag{1}$$

where S is the spin of the Ni(II) ion and J corresponds to the coupling through the μ_3-cabonate anion (Figure 6). The

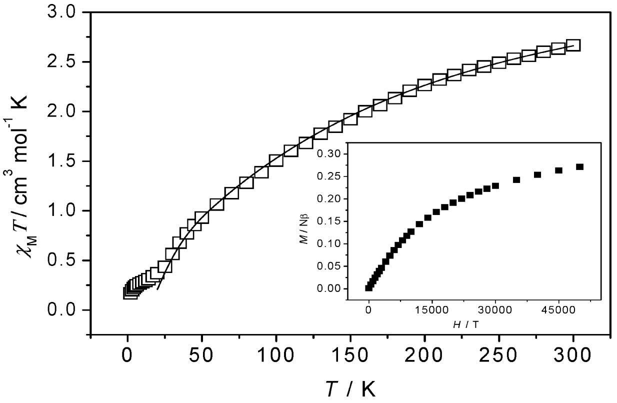

Figure 5. Experimental and calculated (—) variations of $\chi_M T$ vs T of **3**. Inset: magnetization versus H of **3**.

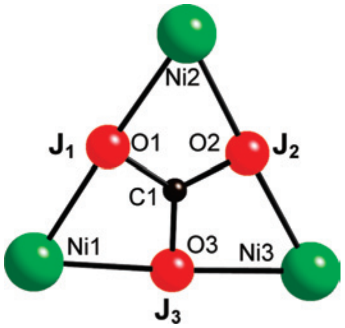

Figure 6. Schematic representation of the magnetic pathways for the trinuclear unit of complex **3**.

free parameters were J (average) and g. The fit has been made by the irreducible tensor operator formalism, using the CLUMAG program.[22] The best agreement was achieved in the temperature range 20−300 K with the magnetic exchange constant $J = -53.1\ \text{cm}^{-1}$, $g = 2.24$, and $R = 1.5 \times 10^{-4}$ ($R = \sum_i(\chi_M T_{i\text{calc}} - \chi_M T_{i\text{exp}})^2/\sum_i(\chi_M T_{i\text{exp}})^2$). The experimental magnetization at 2 K (Figure 5, inset) achieves a value of 0.27 Mβ at 5 T. The change of the slope of the $\chi_M T$ curve versus T, at very low temperatures, could be due to a distortion in the molecular structure of the triangular unit. This anomalous behavior impeded any attempt to calculate the D value (single ion), because at very low temperatures this parameter always led to a decrease in $\chi_M T$. The calculated J values are in good agreement with the structural parameters, taking into account the high Ni−O−Ni angles.[15e]

Conclusion

In this paper, we have shown for the first time that a μ_3-carbonato-bridged triangular heteromolecular species of Ni(II) can be obtained by coordination-driven self-assembly. The role of H-bonding interactions along with the directional coordination bonds are shown to be very important for the self-recognition of different molecular species to be assembled into a specific molecular architecture. We have also isolated a probable intermediate species to have clear insight into the mechanism of CO_2 fixation by the compound in a neutral solution. The variable-temperature magnetic study reveals that the Ni(II) ions are antiferromagnetically coupled in the molecular triangle.

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Supporting Information Available: Crystallographic data in CIF format for the structures reported and additional figures are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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