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Nona- and undecanuclear nickel phosphonate cages

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1. Introduction

Metal phosphonate clusters or cages are attractive owing to their aesthetical structures and potential applications in the fields of biological chemistry [1] and molecular materials science [2] such as single molecular magnets (SMMs) or low-temperature magnetic refrigerants. RPO_3^{2-} (*R* = aryl or alkyl) are good ligands to build such materials because phosphonate can bind many metal ions, compared to carboxylate, to afford various 3d [3], 3d-4f [4] and 4f [5] clusters. There are fewer nickel phosphonate clusters, with only eleven examples found in the literature, due to their low crystallinity [6]. These clusters have Ni₈, Ni₉, Ni₁₀ and Ni₁₂ cores. The cluster nuclearity depends on the phosphonate used (*R* = methyl, t-butyl, phenyl, benzyl, NapCH₂, p-tert-butylphenyl and p-tert-butylbenzyl) and the use of coligands Hchp (6-chloro-2-hydroxypyridine) and Hmhp (6-methyl-2-hydroxypyridine). The magneto-structural correlations were investigated, Ni-O-Ni angles smaller than 99° tend to give ferromagnetic coupling, whereas wider angles favour antiferromagnetic interactions [6a].

In our recent work, we have demonstrated that bulky ligands bearing carbazolyl group could increase the ability of crystallization of the products. This is because the large π -conjugating groups could form strong intermolecular interactions [7]. In the pursuit of new clusters with interesting physical properties, we extend our research on nickel phosphonate. Herein, we report the synthesis,

ABSTRACT

The bulky phosphonate ligands CarbmPO₃H₂ (((9H-carbazol-9-yl)methyl)phosphonic acid) and CarbePO₃H₂ ((2-(9H-carbazol-9-yl)ethyl)phosphonic acid) were employed to construct cages [Ni₉{(py)₂CO₂}₂(CarbmPO₃)₄(^tBuCO₂)₆(tBuCO₂H)₂(CH₃CN)₂] **1** and [Ni₁₁{(py)₂CO₂}₂(CarbePO₃)₄(^tBuCO₂)₆(tBuCO₂H)₂(CH₃CN)₂] **1** and [Ni₁₁{(py)₂CO₂}₂(CarbePO₃)₄(^tBuCO₂)₁₀ (CH₃CN)₂] **2** with (py)₂CO (di-2-pyridyl ketone) and Hpiv (pivalic acid) as coligands under solvothermal conditions. The metallic cores of cages **1** and **2** display vertex-sharing tetragonal pyramidal and tetra-capped octahedral arrangements, respectively. Magnetic property measurements indicate the coexistence of antiferromagnetic and ferromagnetic interactions between nickel centers for both cages. © 2015 Elsevier B.V. All rights reserved.

structural, and magnetic studies of nona- and undecanuclear nickel carbazolyl-phosphonate cages that contain undecanuclear nickel carbazolyl-phosphonate cages that contain two co-ligands $(py)_2CO$ and Hpiv. To the best of our knowledge, compound **2** is the first undecanuclear nickel phosphonate cage, even though a number of Ni₁₁ cages have been reported so far [8].

2. Experimental

2.1. Materials and methods

CarbmPO₃H₂ [9] and [Ni₂(H₂O)(^tBuCO₂)₄(^tBuCO₂H)₄] [10] were prepared according to the literature method. All other starting materials were purchase as reagent grade and used without further purification. Elemental analyses were performed on a Perkin Elmer 240C elemental analyzer. The IR spectra were obtained as KBr disks on a VECTOR 22 spectrometer. The magnetic susceptibility data were obtained on a microcrystalline sample, using a Quantum Design MPMS-XL7 SQUID magnetometer. Diamagnetic corrections were made for both the sample holder and the compound estimated from Pascal's constants [11].

2.2. Synthesis of (2-(9H-carbazol-9-yl)ethyl)phosphonic acid

To carbazole (1.86 g, 11.13 mmol) in dry DMSO (20 mL) NaH (0.49 g, 12.24 mmol) was added, and the solution was stirred for 0.5 h at room temperature under N_2 . Then, diethyl (2-bromoethyl)phosphonate (2.64 g, 12.24 mmol) was added and the





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mixture was heated at 60 °C for 20 h. The reaction mixture was poured into water (100 mL), acidified with 1 M hydrochloric acid and then extracted with ethyl acetate (3×100 mL). The combined organic extracts were washed with brine, dried with magnesium sulfate and the solvent was removed. The residue was dissolved in a minimum amount of ethyl acetate and chromatographic separation on silica was achieved by eluting with pet. ether:ethyl acetate (2:1). The solvent was removed under reduced pressure to give diethyl(2-(9H-carbazol-9-yl)ethyl)phosphonate as pale yellow liquid (1.37 g, 37.02%). To diethyl(2-(9H-carbazol-9-yl)ethyl)phosphonate (3.32 g, 10 mmol) in dry CH₂Cl₂ (20 mL) trimethylsilyl bromide (2.90 mL, 22 mmol) was added under N₂. The solution was stirred for 6 h before being guenched with MeOH and stirred vigorously. After a further 2 h stirring the solvent was removed under reduced pressure and water (5 mL) was added. The mixture was then concentrated under reduced pressure. This step was repeated four times to give (2-(9H-carbazol-9-vl)ethvl)phosphonic acid as an off-white solid. The solid was recrystallized with water to give the white solid (2.91 g, 90.94%). ¹H NMR (DMSO, 400 MHz): 8.16 (d, 2H, J=8.0 Hz), 7.56 (d, 2H, J=12 Hz), 7.48 (t, 2H, *I* = 8.0 Hz), 7.22 (t, 2H, *I* = 8.0 Hz), 4.50–4.54 (m, 2H), 2.01–2.09 (m, 2H) ppm. ¹³C NMR: 139.85, 126.32, 122.73, 120.88, 119.42, 109.39, 37.83, 28.40 ppm. ³¹PNMR: 24.05 (s). Anal. Calc. for C₁₄H₁₄ NO₃P: C, 61.09; H, 5.13; N, 5.09. Found: C, 60.88; H, 5.00; N, 5.20%. IR (KBr, cm⁻¹): 3415.3(s), 3048.7(w), 1618.9(vs), 1457.9(s), 1328.3 (w), 1256.6(m), 1179.6(s), 1130.2(m), 1028.1(s), 950.4(s), 745.6(s), 721.9(s), 616.9(s), 499.6(s).

2.3. Synthesis of

$[Ni_9{(py)_2CO_2}_2(CarbmPO_3)_4(^tBuCO_2)_6(^tBuCO_2H)_2(CH_3CN)_2]$ **1**

CarbmPO₃H₂ (0.0261 g, 0.1 mmol) and $[Ni_2(H_2O)({}^{t}BuCO_2)_4$ (${}^{t}BuCO_2H)_4$] (0.1 g, 0.1 mmol) were dissolved in MeCN (18 mL) and stirred for 20 h. To this was added (py)₂CO (0.015 g, 0.081 mmol) and keep on stirring for another 4 h. The resulting solution was transferred into a 20 mL Teflon-lined autoclave and heated at 120 °C for 48 h, then cooled to room temperature at a rate of 0.1 °C min⁻¹. Green block crystals of **1** were collected. Yield: 46% (based on Ni). *Anal.* Calc. for C₁₃₆H₁₆₃N₁₉Ni₉O₃₂P₄: C, 50.60; H, 5.09; N, 8.24. Found: C, 50.32; H, 4.78; N, 8.01%. IR (KBr, cm⁻¹): 2956.2(w), 2923.4(w), 1628.80(vs), 1578.5(vs), 1481.9(s), 1460.2 (s), 1418.7(s), 1325.2(s), 1229(m), 1170.7(s), 1080.0(s), 995.8(s), 891.04(m), 749.7(s), 551.4(w).

2.4. Synthesis of [Ni₁₁{(py)₂CO₂}₂(CarbePO₃)₄(^tBuCO₂)₁₀(CH₃CN)₂] **2**

CarbePO₃H₂ (0.0275 g, 0.1 mmol) and $[Ni_2(H_2O)({}^{t}BuCO_2)_4$ (${}^{t}BuCO_2H)_4]$ (0.2 g, 0.2 mmol) were dissolved in MeCN (18 mL) and stirred for 20 h. To this was added (py)₂CO (0.015 g, 0.081 mmol) and keep on stirring for another 4 h. The resulting solution was transferred into a 20 mL Teflon-lined autoclave and heated at 120 °C for 48 h, then cooled to room temperature at a rate of 0.1 °C min⁻¹. Green block crystals of **2** were collected. Yield: 55% (based on CarbePO₃H₂). *Anal.* Calc. for C₁₃₄H₁₆₃N₁₁Ni₁₁O₃₆P₄: C, 49.17; H, 5.02; N, 4.71. Found: C, 49.01; H, 4.85, N, 4.90%. IR (KBr, cm⁻¹): 2956.7(m), 2866.5(w), 1567.0(vs), 1507.7(vs), 1421.2 (vs), 1230.5(s), 1177.8(w), 1153.7(w), 1036.4(s), 999.6(s), 749.1(s).

2.5. Crystallography

Single crystals of dimensions $0.25 \times 0.20 \times 0.15 \text{ mm}^3$ for **1**, $0.24 \times 0.18 \times 0.14 \text{ mm}^3$ for **2** were used for structural determinations on a Bruker APEX-II diffractometer using graphite monochromatized Mo K α radiation ($\lambda = 0.71073 \text{ Å}$) at room temperature. Cell parameters were refined by using the program Bruker SAINT on all observed reflections. The collected data were reduced by using

the program Bruker SAINT, and an absorption correction (multi-scan) was applied. The reflection data were also corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined on F^2 by full matrix least squares using SHELXTL. All of the non-hydrogen atoms were located from the Fourier maps, and were refined anisotropically. All H atoms were refined isotropically, with the isotropic vibration parameters related to the non-H atom to which they are bonded. The structure of compounds 1 and 2 contains solvent-accessible voids; hence, the SOUEEZE [12] module of the program suite PLATON was used to generate a fresh reflection file. The void volume and void count electrons are 2551 and 417 for 1, 644 and 56 for 2, which indicate the presence of nine CH₃CN and one CH₃CN molecules in each molecules. The crystallographic and refinement details are listed in Table 1. Selected bond lengths and angles are given in Tables S1-S4, respectively.

3. Results and discussion

3.1. Synthesis

Both complexes follow a general synthetic procedure of reacting $[Ni_2(H_2O)(^tBuCO_2)_4(^tBuCO_2H)_4]$ with RPO_3H_2 (R = Carbm, Carbe) and (py)₂CO in MeCN under solvothermal condition. The mole ratio of starting reactants has impacts on the formation of the final products. If $[Ni_2(H_2O)(^tBuCO_2)_4(^tBuCO_2H)_4]$ is reacted with CarbmPO₃H₂ and (py)₂CO in a 1:1:0.8 M ratio crystals of **1** formed. Changing the reactants' molar ratio we obtain very fine green crystals. While, replacing CarbmPO₃H₂ with CarbePO₃H₂ in the 1:1:0.8 mole ratio we obtained several green crystals with pale precipitate. X-ray determination shows that the green crystal has the same core to 1. Pure crystals of 2 were formed when the ratio is 1:2:0.8. When (2-(9H-carbazol-9-yl)propyl)phosphonic acid was used in the reaction system, no good crystals formed. The coligand (py)₂CO shows the doubly deprotonated anion gem-diol form $((py)_2CO_2^{2-})$ in both cages [13] The trying to obtain hemiketal form [(py)₂C(OR)(OH)] of (py)₂CO in other solvents such as MeOH does not succeed. Ligand (py)₂CO is important for the formation of title nickel clusters. Without (py)₂CO, clusters Ni₁₂ and Ni₈ would be obtained with similar cores to the reported ones [6]. The stability for both compounds were checked. When exposed on the air, compound 1 lost its crystallinity, while compound 2 could keep the crystallinity.

Table 1			
Crystal data a	nd structure	refinement for	1 and 2.

	1	2
Formula	$C_{136}H_{163}N_{19}Ni_9O_{32}P_4\\$	$C_{134}H_{163}N_{11}Ni_{11}O_{36}P_4 \\$
Formula weight	3227.99	3273.30
crystal system	monoclinic	monoclinic
Space group	P2 ₁ /c	$P2_1/n$
a (Å)	19.0523(9)	19.865(4)
b (Å)	19.3651(9)	16.906(3)
c (Å)	23.4670(11)	23.589(5)
β (°)	113.1180(11)	106.31(3)
Ζ	2	2
D_{calc} (g cm ⁻³)	1.192	1.412
μ (mm ⁻¹)	1.141	1.444
Total/unique reflections	59611/14494	61795/13370
Observed data $[I > 2.0\sigma(I)]$	7307	9383
R _{int}	0.099	0.109
Goodness-of-fit (GOF) F ²	1.046	1.067
$R_1, wR_2 [I > 2.0\sigma(I)]^a$	0.0604, 0.1557	0.0746, 0.1501
R_1 , w R_2 (all data)	0.1231, 0.1739	0.1174, 0.1689
(Δho) maximum, (Δho)	-0.39, 0.41	-0.53, 0.86
minimum (e Å ⁻³)		

^a $R_1 = \Sigma ||F_0| - |F_c| / \Sigma |F_0|$; $wR_2 = \{ \Sigma w (F_0^2 - F_c^2)^2 / \Sigma w (F_0^2)^2 \}^{1/2}$.

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