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ARTICLE

Templated Self-Assembly and Crystal Structure of Methyl Pamoate and its Polynuclear Clusters with Nickel(II) and Barium(II)

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ABSTRACT

The synthesis and X-ray crystal structure of methyl pamoate and double templated self-assembly and crystal structure of new polynuclear nickel(II)/barium(II) cluster with methyl pamoate is reported. Methyl pamoate was prepared by refluxing pamoic acid (m.f. $C_{23}H_{16}O_6$)with thionyl chloride to get pamoyl chloride and then refluxing this pamoyl chloride with methanol. Methyl pamoate was further used to get Ni(II)/Ba(II)-polynuclear complex by refluxing with $Ni(ClO_4)_2\cdot 6H_2O$ and $Ba(ClO_4)_2\cdot 3H_2O$ and this complex was characterized by elemental analysis, FTIR. Methyl pamoate and its complex with nickel(II)/barium(II) were crystallized by vapour diffusion method and crystals were characterized by a single crystal X-ray diffraction study. Polynuclear nickel(II)/barium(II) cluster with methyl pamoate crystallized in the triclinic space group P-1, with unit cell parameters $a = 19.0613$ Å , $b = 19.2428$ Å , $c = 26.1916$ Å , $\alpha = 111.0657°$, $\beta = 111.1175°$, $\gamma = 118.0667°$, $V = 6059.009$ Å^3, $Z = 6$. The cluster contains three nickel(II) atoms and one barium(II) atom and these are coordinated by four molecules of methyl pamoate. Methyl pamoate crystallized in the trigonal space group P3(2)21, with unit cell parameters $a = 10.5069$ Å , $b = 10.5069$ Å , $c = 15.5909$ Å , $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$, $V = 1490.56$ Å^3, $Z = 3$.

KEYWORDS

Pamoyl ester, Polynuclear cluster, Double template, Methyl pamoate.

INTRODUCTION

Barium is surprisingly abundant in the earth's crust, being the 14th most abundant element. High amounts of barium may only be found in soils and in food, such as nuts, seaweed, fish and certain plants. Since the pioneering work of Tomic [1] in 1965 and Hoskins and Robson [2] in the 1990s on a new class of solid polymeric materials, currently known as metal-organic frameworks (MOF) or coordination polymers, mono- and polynuclear coordination compounds in which metal centers are connected by organic linkers have become important in various research areas [3,4]. Currently, these compounds are of great interest due to their potential practical applications [5-21]. Binuclear organometallic complexes of nickel(II), zinc(II), cobalt(II) and manganese(II) were found to be important intermediates in biological systems which catalyze the hydrolysis

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of a range of peptide and phosphate ester bonds *via* the formation of O–P–O bridged organometallic derivatives [22]. These species play a central role in biological processes of oxidative phosphorylation [23,24], oxidative decarboxylation [25] and energy transduction [26-28]. From the viewpoint of materials chemistry, organic-inorganic hybrids are an important class of compounds in advanced materials design [29-34].

However, currently, no examples of polynuclear nickel-barium complex with methyl pamoate ligand is known. Here, we describe the synthesis and crystal structure of new polynuclear nickel-barium complex based on methyl pamoate ligand.

EXPERIMENTAL

All the reagents and solvents employed were commercially available and used as received without further purification. IR spectra were performed using KBr pellets on a Perkin Elmer Paragon 1000PC. CHN analysis was performed using a CE-440 Elemental analyzer. ^{1}H NMR was performed using a Bruker Avance 400. Mass spectra were recorded on a Thermo Fisher Exactive + Triversa Nanomate mass spectrometer. Data collection for X-ray crystallography was completed using a Bruker APEX2 CCD diffractometer and data reduction was performed using Bruker SAINT. SHELXTL was used to solve and refine the structure.

Synthesis of methyl pamoate: 2.992 g (7.71 mmol) pamoic acid (m.f. $C_{23}H_{16}O_6$) and 25 mL of thionyl chloride was taken in 100 mL pre-dried round-bottomed flask forming a yellow suspension. Then the reaction was set-up for reflux with stirring for 16 h in a fuming cupboard. After 16 h the flask showed an orange/red product (pamoyl chloride). The flask was then allowed to cool to room temperature before the removal of the majority of the solvent. Then the solvent was removed by using rotary evaporator in fuming cupboard to get orange solid (pamoyl chloride). 30 mL methanol was added into the orange solid forming a light orange coloured solution and the mixture was refluxed for 45 min to complete the reaction getting the yellow solid (methyl pamoate) (**Scheme-I**). Then it was cooled and filtered.

Yield was 2.231g, 69.5 %. Elemental analysis calculated for $C_{25}H_{20}O_6(H_2O)$: C 69.12 %; H 5.1 %; Observed: C 69.59 %; H 4.57 %. ^{1}H NMR ($CDCl_3$ as solvent, δ in ppm): 3.975 (s, 6H, OMe), 4.88 (s, 2H, CH_2), 7.12 (t, 2H, ArH), 7.3 (t, 2H, ArH), 7.62 (d, 2H, ArH), 8.18 (d, 2H, ArH), 8.32 (s, 2H, ArH), 11.2 (s, 2H, OH). IR (ATR, cm^{-1}): 1670.93[s, (C = O)], 3164 [b, (O-H H-bonded)]. ESI-MS (*m/z*, rel. intensity, assignment): 417 (77 %) $[M+H]^+$, 850 (100 %) $[M_2+NH_4]^+$.

Synthesis of Ni(II)/Ba(II)-polynuclear complex based on methyl pamoate: About 0.1 g (0.2403 mmol) methyl pamoate was dissolved in 10 mL chloroform and was mixed with 0.088 g (0.2403 mmol) $Ni(ClO_4)_2.6H_2O$ and 0.0235 g (0.06022 mmol) $Ba(ClO_4)_2·3H_2O$ taken in a round bottomed flask containing 40 mL methanol. This mixture was heated under reflux for 45 min and the methanolic solution of Et_3N (1 mL in minimum amount of methanol) was added to the refluxing solution *via* pipette. Then it was refluxed for further 20 h. It was filtered to get a solid powder after cooling at room temperature. This powder was characterized by different spectroscopic techniques and was tried to crystallize by vapour diffusion method using DMF and diethyl ether.

Yield was 0.067g, 55.83 %. Elemental analysis calculated for $C_{100}H_{72}O_{24}Ni_3Ba (ClO_4)_2$: C 55.35 %, H 3.34 %; Observed: C 55.37 %, H 4.00 %. IR (KBr-Pellet, cm^{-1}): 3401, 2951, 1654, 1619, 1579, 1546, 1505, 1489, 1448, 1425, 1382, 1337, 1298, 1240, 1208, 1161, 1091, 1045, 1023, 981, 900, 795, 743, 552, 455.

RESULTS AND DISCUSSION

Methyl pamoate was prepared by refluxing pamoic acid with thionyl chloride to get pamoyl chloride and then refluxing this pamoyl chloride with methanol. This methyl pamoate was crystallized by vapour diffusion method. Crystal structure data (Table-1) shows that it has hydrogen bond between phenolic hydrogen and carbonyl oxygen (Fig. 1, Tables 2 and 3).

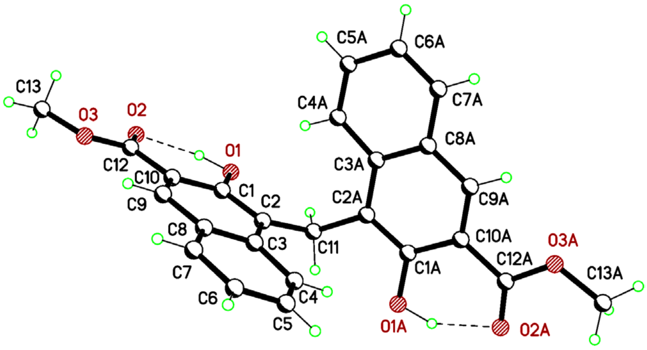
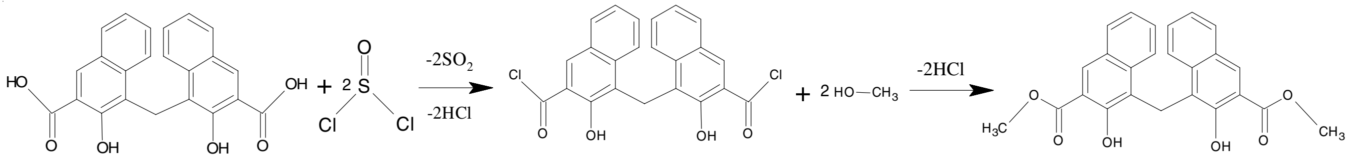


Fig. 1. X-ray crystal structure of methyl pamoate

Ni(II)/Ba(II) complex of methyl pamoate was prepared by refluxing methyl pamoate with $Ni(ClO_4)_2·6H_2O$ and $Ba(ClO_4)_2·3H_2O$ and this complex was characterized by elemental analysis and FTIR. Methyl pamoate and its complex were crystallized by vapour diffusion method and crystals were characterized by single crystal X-ray diffraction study.

The generality of the double template effect (in which both metal ions are essential for the assembly) has been demonstrated by characterization of the assembly of a Ni(II)/Ba(II) complex of the methyl pamoate. In this case the resulting complex is less symmetric but the main features of the self-assembly process are produced. *i.e.* the Ba(II) ion assembles the phenolate ligands and the Ni(II) ions lock them together.

The crystal structure consists of hetro-nuclear complex of nickel and barium based on methyl pamoate. Complex



Scheme-I: Synthesis of methyl pamoate

TABLE-1
CRYSTAL DATA AND STRUCTURE
REFINEMENT FOR METHYL PAMOATE

Identification code	Methyl pmoate
Empirical formula	$C_{25}H_{20}O_6$
Formula weight	416.41
Temperature	150 (2) K
Wavelength	0.71073 Å
Crystal system	Trigonal
Space group	P3 (2)21
Unit cell dimensions	a = 10.5069 (6) Å; α = 90°
	b = 10.5069 (6) Å; β = 90°
	c = 15.5909 (9) Å; γ = 120°
Volume	1490.56 (15) $Å^3$
Z	3
Density (calculated)	1.392 Mg/m^3
Absorption coefficient	0.100 mm^{-1}
F(000)	654
Crystal size	0.31 × 0.30 × 0.30 mm^3
Crystal description	Yellow block
Theta range for data collection	2.24 to 28.34°.
Index ranges	-14< = h< = 14,
	-14< = k< = 13,
	-20< = l< = 20
Reflections collected	15295
Independent reflections	1428 [R(int) = 0.0287]
Completeness to theta = 28.34°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9707 and 0.9698
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1428/0/144
Goodness-of-fit on F^2	1.059
Final R indices [I>2σ(I)]	R1 = 0.0314, wR2 = 0.0885
R indices (all data)	R1 = 0.0343, wR2 = 0.0920
Absolute structure parameter	0 (10)
Largest diff. peak and hole	0.216 and -0.155 e. $Å^{-3}$

TABLE-2
BOND LENGTHS (Å) AND ANGLES (°)
FOR METHYL PAMOATE

O(1)-C(1)	1.361 (2)	O(1)-C(1)-C(2)	118.56 (14)
C(1)-C(2)	1.385 (2)	O(1)-C(1)-C(10)	120.29 (14)
C(1)-C(10)	1.430 (2)	C(2)-C(1)-C(10)	121.12 (14)
C(2)-C(3)	1.427 (2)	C(1)-C(2)-C(3)	118.74 (14)
C(2)-C(11)	1.519 (2)	C(1)-C(2)-C(11)	119.45 (14)
C(3)-C(4)	1.426 (2)	C(3)-C(2)-C(11)	121.81 (13)
C(3)-C(8)	1.426 (2)	C(4)-C(3)-C(8)	117.29 (15)
C(4)-C(5)	1.366 (3)	C(4)-C(3)-C(2)	122.85 (15)
C(5)-C(6)	1.411 (3)	C(8)-C(3)-C(2)	119.85 (15)
C(6)-C(7)	1.364 (3)	C(5)-C(4)-C(3)	120.93 (16)
C(7)-C(8)	1.421 (2)	C(4)-C(5)-C(6)	121.62 (17)
C(8)-C(9)	1.404 (2)	C(7)-C(6)-C(5)	119.06 (17)
C(9)-C(10)	1.372 (2)	C(6)-C(7)-C(8)	121.08 (16)
C(10)-C(12)	1.473 (2)	C(9)-C(8)-C(7)	120.57 (15)
C(11)-C(2)#1	1.519 (2)	C(9)-C(8)-C(3)	119.38 (15)
C(12)-O(2)	1.221 (2)	C(7)-C(8)-C(3)	120.00 (15)
C(12)-O(3)	1.331 (2)	C(10)-C(9)-C(8)	120.95 (14)
O(3)-C(13)	1.448 (2)	C(9)-C(10)-C(1)	119.74 (14)
		C(9)-C(10)-C(12)	120.91 (14)
		C(1)-C(10)-C(12)	119.35 (14)
		C(2)-C(11)-C(2)#1	115.13 (19)
		O(2)-C(12)-O(3)	122.29 (15)
		O(2)-C(12)-C(10)	124.64 (15)
		O(3)-C(12)-C(10)	113.06 (14)
		C(12)-O(3)-C(13)	116.29 (14)

Symmetry transformations used to generate equivalent atoms: #1 y,x,-z+1

TABLE-3
HYDROGEN BONDS FOR METHYL PAMOATE (Å AND °)

D–H···A	d(D-H)	d(H···A)	d(D···A)	∠(DHA)
O(1)-H(1)···O(2)	0.96 (3)	1.72 (2)	2.6044 (18)	151 (2)

Symmetry transformations used to generate equivalent atoms: #1 y,x,-z+1

contains four molecules of methyl pamoate, three nickel(II) atoms and one barium(II) atom (Fig. 2). Each nickel is six coordinated. Two of the three nickels are in same coordination environment and one nickel is in different coordination environment. Each of the two nickel atoms having similar environment is bridging between three ligands and each is coordinated by three phenolic oxygen atoms (one from each ligand) and three carbonyl oxygen atoms (one from each ligand). The third nickel atom having different environment is bridging between two ligands and is coordinated by two phenolic oxygen atoms (one from each ligand), two carbonyl oxygen atoms (one from each ligand), one nitrogen atom from DMF and it is also connected with barium through –OH bridge. Barium is in the centre with coordination number nine and is coordinated by seven phenolic oxygen atom (two from each three of the four ligands and one from one of the four ligands), one DMF and also connected with nickel (having different coordination environment) through –OH. Geometry around each Nickel atom is octahedral and the geometry around barium atom is trigonal prismatic.

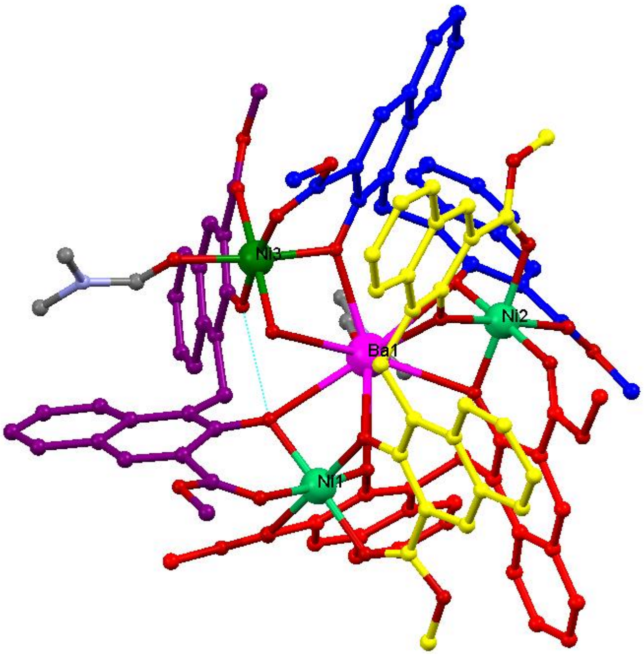


Fig. 2. X-ray crystal structure of polynuclear clusters of nickel(II)/barium(II) based on methyl pamoate

IR spectra of the cluster (Fig. 3) shows peak at 3401, 2951, 1654, 1619, 1579, 1546, 1448, 1425, 1382, 1337, 1298, 1240, 1208, 1161, 1091, 1045, 1023, 981, 795, 743 and 455 cm^{-1}.

Conclusion

In the synthesis of polynuclear nickel(II)/barium(II) cluster with methyl pamoate ligand, the generality of the double template effect (in which both metal ions are essential for the assembly) has been demonstrated by characterization of the assembly

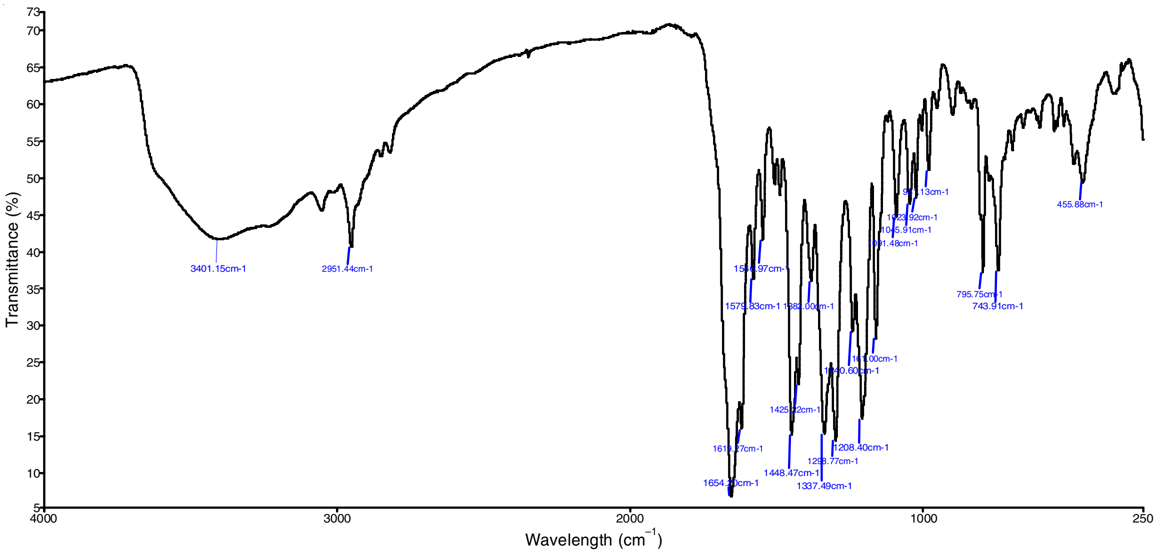


Fig. 3. IR spectra of nickel(II) and barium(II) complex based on methyl pamoate

of a Ni(II)/Ba(II) complex of the methyl ester of pamoic acid. In this case, the resulting complex is less symmetric but the main features of the self-assembly process are reproduced, *i.e.* the Ba(II) ion assembles the phenolate ligands and the Ni(II) ions lock them together. Methyl pamoate shows hydrogen bond between phenolic hydrogen and carbonyl oxygen.

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