Hydroxyl-directed dinitration of carboxylate ligands mediated by lead and nickel nitrates and preparation of Pb/Ni heterometallic complexes under hydrothermal conditions†

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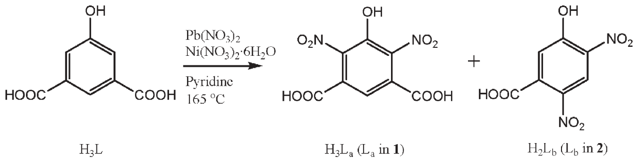
The hydrothermal reaction of 5-hydroxyisophthalic acid (H_3L) and lead and nickel nitrates produced a heterometallic polymer $[Pb_6Ni(\mu_3\text{-}OH)_8(L_a)_2]_n$ containing heptanuclear $[Pb_6Ni(\mu_3\text{-}OH)_8]^{6+}$ units and a homometallic complex $\{[Pb(L_b)(H_2O)]\cdot(H_2O)_{0.25}\}_n$ consisting of one-dimensional lead-oxide chains: evidently, the L_a and L_b ligands resulted from *in situ* hydroxyl-directed dinitration of L ligand during the hydrothermal reaction.

Much effort has been devoted to the synthesis and characterization of heterometallic coordination complexes, with the motivation for this research stemming from their favorable thermal stability and remarkable structural diversity as well as potential applications in magnetism, luminescence and heterogeneous catalysis.[1] However, in contrast to employing different transition metals or mixed rare earth and transition metal-oxide clusters or chains,[2] the mixed use of heavy main group and transition metal-oxide subunits to synthesize heterometallic polymers is extremely rare. Considering their large radius, strong affinity for oxygen atoms and rich coordination numbers and geometries, heavy metal ions are especially suitable for generating metal-oxide clusters and chains, as evidenced by lead-carboxylate or -phosphate coordination compounds.[3] In view of synthetic strategies, solvo- and hydrothermal techniques have been widely applied in the preparation of oxide-based materials, such as zeolites, arsenates and germinates besides carboxylates and phosphates,[4] moreover, they represent important methods in the discovery of peculiar organic reactions and *in situ* synthesis of bridging ligands because of the relatively high temperature and pressure compared with traditional synthetic methods.[5] In this communication, we wish to report a new example of the dinitration of an organic ligand and the preparation of Pb/Ni heterometallic complexes under hydrothermal conditions.

The hydrothermal reaction of 5-hydroxyisophthalic acid (H_3L), $Pb(NO_3)_2$ and $Ni(NO_3)_2\cdot6H_2O$ produced two complexes,‡ a heterometallic polymer $[Pb_6Ni(\mu_3\text{-}OH)_8(L_a)_2]_n$ (**1**) (H_3L_a = 4,6-dinitro-5-hydroxyisophthalic acid) and a homometallic complex $\{[Pb(L_b)(H_2O)]\cdot(H_2O)_{0.25}\}_n$ (**2**) (H_2L_b = 2,4-dinitro-5-hydroxybenzoic acid). During the generation of products, two kinds of dinitration reactions of the deprotonated H_3L were observed, and a decarboxylation process also occurred for the synthesis of **2** (Scheme 1). To the best of our knowledge, there has been no report of the dinitration of the original organic ligands mediated by the coexisting heavy main group and transition metal nitrates under hydrothermal conditions, although some nitrate-catalyzed mono- and polynitrations of aromatic compounds have been accomplished under different conditions.[6]



Scheme 1

The heterometallic complex **1**§ is a three-dimensional network consisting of hydroxyl-bridged heptanuclear heterometallic clusters, in which L_a is a product of hydroxyl-directed *o*-dinitration. The heptanuclear $[Pb_6Ni(\mu_3\text{-}OH)_8]^{6+}$ unit is composed of corner-fused double cubanes, in which two $[Pb_3(\mu_3\text{-}OH)_4]$ cores share one Ni^{II} ion (Fig. 1a). This heptanuclear structural motif was also observed in transition metal and alkaline earth metal coordination polymers.[7] However, reports about the heptanuclear Ni–Pb-unit are still rare, with only three examples containing dinuclear and trinuclear Ni–Pb-units known.[8] The Ni^{II} atom is located on the inversion center of the corner-fused double cubanes, surrounded by six μ_3-OH groups in a slightly distorted octahedral coordination environment. The bond lengths of $Ni1–O_{(hydroxyl)}$ range from 1.995(8) to 2.138(8) Å. All of the Pb^{II} atoms are five-coordinated in

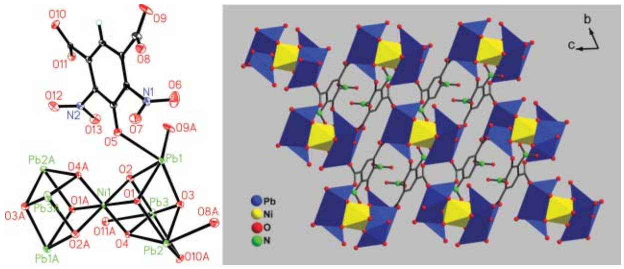


Fig. 1 (a) Perspective view of the asymmetric unit of **1** and the heptanuclear $[Pb_6Ni(\mu_3\text{-}OH)_8]^{6+}$ unit with 30% probability ellipsoids. (b) View of the three-dimensional structure of **1**, in which the nitro groups have been shown.

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† Electronic supplementary information (ESI) available: Synthesis of complex **3**; more structural figures and descriptions of **3**, mass spectra for **1** and the reaction solution. See DOI: 10.1039/b600684a

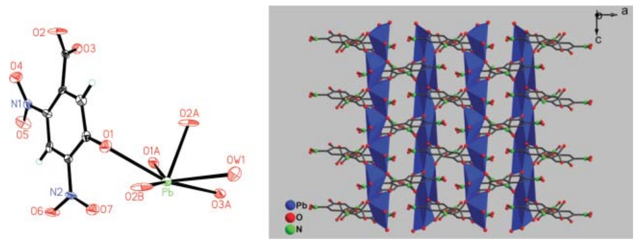

Fig. 2 (a) Perspective view of the coordination geometry of the Pb^{II} center and the L_b ligand with 30% probability ellipsoids, free water molecule was omitted for clarity. (b) View of the two-dimensional layer in **2**, in which the nitro groups have been shown.

a *hemidirected* trigonal bipyramidal geometry.[9] The Pb1 is surrounded by three μ_3-OH groups, one carboxylate oxygen atom and one deprotonated hydroxyl group of different L_a, while both Pb2 and Pb3 are coordinated by three μ_3-OH groups and two carboxylate oxygen atoms of different L_a. In L_a, the C–N bond distances (1.41(1) Å for C8–N1 and 1.47(1) Å for C6–N2) are close to those observed in nitrobenzene,[10] and are shorter than the C–C bond distances of carboxylate groups located in the benzene ring. The N–O bond distances are in the range from 1.19(1) to 1.24(1) Å, which are characteristic of the nitro group. Owing to no coordination of the nitro group, the L_a acts as a μ_6-bridge linking six Pb^{II} atoms through a deprotonated hydroxyl group, one μ_2,η^3-carboxylate group and one μ_2,η^2-carboxylate group (Fig. S1†). As a result, the heptanuclear heterometallic clusters are extended into a three-dimensional structure through L_a spacers (Fig. 1b).

The homometallic complex **2**§ is a three-dimensional supramolecular architecture containing one-dimensional lead-oxide chains. The asymmetric unit of **2** contains one unique Pb^{II} atom, one L_b, one coordinated water molecule and one-quarter of a free water molecule (Fig. 2a). The L_b is a product of hydroxyl-directed *o*-,*p*-dinitration and subsequent decarboxylation. The C–N bond distances are 1.450(6) Å for C3–N1 and 1.444(6) Å for C5–N2, the N–O bond distances range from 1.230(6) to 1.232(5) Å, and the bond angles of O5–N1–O4 and O6–N2–O7 are 124.0(5)° and 121.0(4)°, respectively, all of the parameters are consistent with those of the nitro group in the benzene ring.[8] The nitro groups in **2**, different from that in **1**, are involved in hydrogen bonding interactions with coordinated water molecules. The Pb^{II} center is in a *hemidirected* octahedral geometry,[9] surrounded by six oxygen atoms from deprotonated hydroxyl and carboxylate groups of different L_b and one coordinated water molecule. The Pb–O bond distances range from 2.450(4) to 2.662(5) Å, and the Pb–OW1 bond distance is 2.55(1) Å. The L_b behaves as a μ_5-bridge connecting five Pb^{II} atoms through one deprotonated hydroxyl bridge and one μ_2,η^3-carboxylate group (Fig. S2†). Pb^{II} centers are connected by the coordinating groups of L_b to give rise to a one-dimensional lead-oxide chain, in which the nearest Pb···Pb distance is 4.064 Å (Fig. S3†). The L_b spacers stretch the one-dimensional chain into a two-dimensional layer with void spaces, where the uncoordinated nitro groups are situated (Fig. 2b). The extensive hydrogen bonding interactions further extend the two-dimensional layer into a three-dimensional supramolecular architecture (Fig. S4†).

The nitration of aromatic compounds is a fundamental and important reaction in organic synthesis. The orientation of the nitro group on the benzene ring is strongly affected by the electron-donating and electron-withdrawing substituents.[11] In the case of dinitration reactions, certain electron-donating substituents, such as hydroxyl and methoxyl groups, as *ortho–para* directing groups, can preferentially give rise to a mixture of *o*-dinitro and *o*-,*p*-dinitro products; while the electron-withdrawing substituents, such as aldehyde, carboxyl and nitro groups, as *meta* directing groups, can easily direct to *m*-nitro products. Consequently, according to the *ortho–para* directing rule of the hydroxyl group, two kinds of dinitro products of the L ligand (*o*-dinitro product in **1**, *o*- and *p*-dinitro product in **2**) were observed, as described above. Since the *meta* position is occupied by a strongly activating hydroxyl group, the *meta* directing effect of the moderately deactivating carboxylate groups may be neglected. It should be mentioned that the *o*-,*p*-dinitro product of L ligand was unstable owing to the presence of four adjacent electron-withdrawing groups, therefore, the carboxylate group between the two strong electron-withdrawing nitro groups was further eliminated to produce the stable L_b ligand in **2** under the hydrothermal conditions.

Due to the relatively forcing conditions,[5a] the detailed investigation of the hydrothermal reaction mechanism presents a significant challenge. In order to evaluate whether both lead and nickel nitrates played crucial roles in the reaction process, several tests were carried out: (i) using either $Pb(OAc)_2$ or $NiCl_2 \cdot 6H_2O$ instead of $Pb(NO_3)_2$ and $Ni(NO_3)_2 \cdot 6H_2O$, the same results were not observed; (ii) using $Pb(NO_3)_2$ as a reactant under identical conditions, complex **3** $\{[Pb_{1.5}(L)] \cdot (H_2O)_{1.5}\}_n$ (see Supporting Information Fig. S5–S8†) was isolated exclusively, in which the organic ligand was not nitrified; (iii) using $Ni(NO_3)_2 \cdot 6H_2O$ as a reactant, green depositions were formed, where no nitrogen element was observed as determined by elemental analysis, which suggests that no nitration has occurred. Therefore, it can be concluded that the dinitration of L ligand resulted from synergetic effects of both $Pb(NO_3)_2$ and $Ni(NO_3)_2 \cdot 6H_2O$ under hydrothermal conditions.

In summary, the hydroxyl-directed dinitration of 5-hydroxyisophthalic acid led to the synthesis of Pb/Ni heterometallic coordination polymers. Two novel coordination polymers from *o*-dinitro and *o*-,*p*-dinitro products, respectively, were successfully isolated. **1** is a heterometallic polymer with rare heptanuclear $[Pb_6Ni(\mu_3\text{-}OH)_8]^{6+}$ units. In addition to the dinitration of the organic ligand, a decarboxylation also occurred in **2**. This work has demonstrated that the synergetic effects of $Pb(NO_3)_2$ and $Ni(NO_3)_2 \cdot 6H_2O$ are essential for dinitration of the deprotonated 5-hydroxyisophthalic acid and the preparation of heterometallic polymers under hydrothermal conditions. The clarification of the mechanism of dinitration and decarboxylation as well as the origin of the synergy between $Pb(NO_3)_2$ and $Ni(NO_3)_2 \cdot 6H_2O$ under hydrothermal conditions requires further studies, which are currently underway in our laboratory.

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Notes and references

‡ Syntheses of **1** and **2**: a mixture of $Pb(NO_3)_2$ (0.50 mmol, 165.6 mg), $Ni(NO_3)_2 \cdot 6H_2O$ (0.40 mmol, 116.3 mg) and 5-hydroxyisophthalic acid (0.25 mmol, 45.5 mg) in 18 mL H_2O was stirred for 20 min, then the pH

value was adjusted to 5 by pyridine. After stirring for another 20 min, the mixture was transferred to a Teflon-lined stainless steel vessel and heated to 165 °C for 72 h, then the reaction system was cooled to room temperature during 48 h. Red block crystals of **1** (yield: 15.7 mg, 9% based on Pb) and light yellow needle crystals of **2** (yield: 87.5 mg, 38% based on Pb) were obtained. Elemental analysis (%): calc. for **1** $C_{16}H_{10}Pb_6NiN_4O_{26}$ (1976.13): C 9.72, H 0.51, N 2.83; found: C 9.86, H 0.56, N 2.60. IR (KBr, cm^{-1}): 3465 (bs), 1568 (s), 1497 (m), 1384 (s), 1262 (m), 1044 (m), 887 (m), 780 (s), 733 (m), 650 (w). Elemental analysis (%): calc. for **2** $C_7H_{4.5}PbN_2O_{8.25}$ (455.82): C 18.44, H 0.99, N 6.14; found: C 18.23, H 1.02, N 6.05. IR (KBr, cm^{-1}): 3524 (bs), 1564 (s), 1504 (m), 1435 (m), 1383 (m), 1337 (s), 1262 (m), 1140 (w), 815 (m), 716 (s), 565 (s). The solution was filtered, then analyzed by mass spectrometry (MS) (FINNIGAN LCQ Deca XP MAX) (Fig. S9†). The mass spectrogram indicated that the cluster structure of **1** was not present in the solution.

§ Crystal data for **1**: M_r = 1976.13, triclinic, space group $P\bar{1}$, a = 8.083(2) Å, b = 9.299(3) Å, c = 10.922(3) Å, α = 67.735(6)°, β = 82.665(9)°, γ = 85.860(8)°, V = 753.2(4) Å^3, Z = 1, T = 293(2) K, ρ_{calc} = 4.357 g cm^{-3}. A total of 5877 reflections were collected, of which 3409 were unique reflections, R(int) = 0.0611, μ(Mo Kα) = 34.132 mm^{-1}, parameters = 241, GOF = 0.994, $R1$ = 0.0392, w$R2$ = 0.0868 ($I \geqslant 2\sigma(I)$) and $R1$ = 0.0464, w$R2$ = 0.0880 for all data. Crystal data for **2**: M_r = 455.82, orthorhombic, space group $Pccn$, a = 12.125(3) Å, b = 23.399(5) Å, c = 7.010(1) Å, V = 1988.8(7) Å^3, Z = 8, T = 293(2) K, ρ_{calc} = 3.045 g cm^{-3}. A total of 14138 reflections were collected, of which 2277 were unique reflections, R(int) = 0.0742, μ(Mo Kα) = 17.011 mm^{-1}, parameters = 178, GOF = 1.039, $R1$ = 0.0272, w$R2$ = 0.0613 ($I \geqslant 2\sigma(I)$) and $R1$ = 0.0346, w$R2$ = 0.0650 for all data. OW1 atom was handled as disordered at two positions (OW1 and OW1′) with occupancy of 0.5. Crystal data for **3**: M_r = 516.93, monoclinic, space group $C2/c$, a = 10.000(9) Å, b = 13.05(1) Å, c = 15.55(1) Å, β = 99.85(1)°, V = 2000(3) Å^3, Z = 8, T = 173(2) K, ρ_{calcd} = 3.433 g cm^{-3}. A total of 5887 reflections were collected, of which 1758 were unique reflections, R(int) = 0.0815, μ(Mo Kα) = 25.260 mm^{-1}, parameters = 154, GOF = 1.048, $R1$ = 0.0481, w$R2$ = 0.1230 ($I \geqslant 2\sigma(I)$) and $R1$ = 0.0695, w$R2$ = 0.2083 for all data. CCDC number 288164 for **1**, 288165 for **2** and 288166 for **3**. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b600684a

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