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Unprecedented tubular channels assemblies afforded by alkyl-substituted oxamide oxime metal complexes

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The synthesis of an oxamide oxime substituted with hexyl chains, together with its nickel(II) (1) and palladium(II) (2) complexes, is described. Both complexes crystallize in the hexagonal space group $R\bar{3}$ (No 148). In the crystal the complex molecules are linked by hydrogen bonds involving the oximic oxygen atoms and the amino nitrogen atoms to build infinite tubular channels partly filled by the hexyl chains and self-organized in two-dimensional hexagonal arrays.

The design of molecule-based organic and inorganic solids, exhibiting pre-defined functions, is an active task in material science.[1] In this field the synthesis of mesoporous materials based on metal-organic open frameworks[2] is the focus of great attention as potentially interesting for numerous applications ranging from molecular absorption,[3] gas storage[4] and heterogeneous catalysis[5] to magnetic,[6] non-linear optic[7] or photonic materials.[8] In the course of our work on metal complexes of alkyl-substituted phthalocyanine[9] and oxamide oxime ligands[10,11] we unexpectedly discovered that the nickel(II) (**1**) and palladium(II) (**2**) complexes of a soluble alkyl substituted oxamide oxime self-assemble through hydrogen bonds to afford metal-organic open frameworks with tubular channels.

The ligand was obtained from the reaction of dichloroglyoxime[12] with an excess of hexylamine at room temperature in ethanol (Scheme 1). Further treatment of the resulting ethanolic solution with water allows the separation of the ligand as a white precipitate from the water -soluble hexylamonium chloride salts. The nickel(II) (**1**) and palladium(II) (**2**) complexes were synthesized by reacting the ligand with $NiCl_2{\cdot}6H_2O$ and Na_2PdCl_4, respectively, in ethanol. Compounds **1** and **2** are isostructural and crystallize in the hexagonal space group $R\bar{3}$. A view of the molecular unit is shown in Fig. 1 in the case of the nickel(II) complex (**1**).

The molecules are centrosymmetric at the metal center. The latter, nickel(II) (**1**) or palladium(II) (**2**), is bound by the four oximic nitrogen atoms of two oxamide oxime ligands and is in a square planar environment. The four hexyl carbon chains are oriented almost perpendicularly to the perfectly planar central core containing the metal ion [M{O1–N1–C1(N3)–C2(N4)–N2–O2}$_2$] [M = Ni(II) (**1**) and Pd(II) (**2**)] (Fig. 1). The M–N(oxime) bond lengths are 1.880(2) and 1.862(2) Å for compound **1**, and 1.965(4) and 1.973(3) Å for compound **2** while the N1–Ni–N2 and N1–Pd–N2 bond angles are 81.66(9)° and 79.1(2)° for compounds **1** and **2**, respectively. In both compounds **1** and **2**, the oximic oxygen atoms (O1 and O2) are intramolecularly hydrogen-bonded as normally observed in the anti isomer metal complexes of *vic*-dioxime. The O1–O2a distances are 2.482(3) and 2.632(4) Å for compounds **1** and **2**, respectively.

The above structural features are in the range previously reported for nickel(II) and palladium(II) complexes of dioxime[13] and oxamide oxime.[11,14] However, these compounds

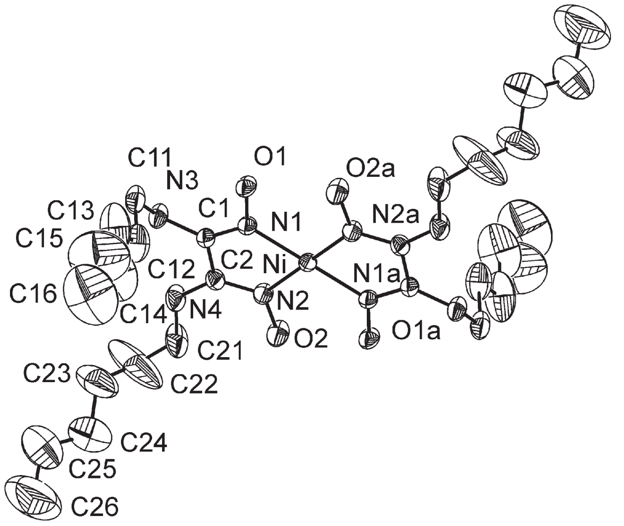
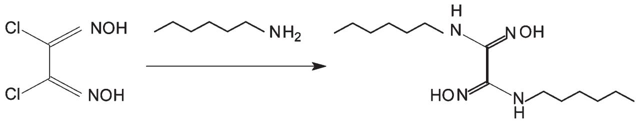


Fig. 1 View of complex **1** with thermal ellipsoid plot at 30% probability level. The hydrogen atoms are omitted for clarity. Selected intramolecular distances (Å): Ni–N1, 1.880(2); Ni–N2, 1.862(2); O1–N1, 1.358(3); O2–N2, 1.389(3); O1–O2a, 2.482(3) for **1** and Pd–N1, 1.973(3); Pd–N2, 1.965(4); O1–N1, 1.342(4); O2–N2, 1.391(4); O1–O2a, 2.632(4) for **2**. Symmetry code a: 1 − *x*, 1 − *y*, −*z*.



Scheme 1 Synthesis of the ligand (H_2L).

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reveal an unprecedented crystal structure when considering the 3D packing. Indeed, the most interesting aspect of these compounds lies in the intermolecular hydrogen bonds formed between the oximic oxygen atoms (O1) and the amino nitrogen atoms [O1···H–N3 = 2.866(3) and O1···H–N4 = 2.991(3) Å for compound **1** and O1–H–N3 = 2.858(5) and O1–H–N4 = 2.922(5) Å for compound **2**]. These hydrogen bonds connect the complex molecules to each other as shown in Fig. 2 and Fig. 3. Due to symmetry operations the 3D extension of this hydrogen bond network affords tubular channels developing along the *c* axis direction and which are interconnected in the *ab* plane (Fig. 3).

These tubular channels are walled by the metal ions of the central core $[M\{O1–N1–C1(N3)–C2(N4)–N2–O2\}_2]$ whose mean plane makes an angle of 55° with the *c* axis direction. The maximum diameter of the tubular channels measured between the walls containing the metal ions is 15.817 and 16.097 Å for compounds **1** and **2**, respectively (Fig. 3). In fact the hexyl chains partially fill the void within the channels (Fig. 4) and the remaining free space of the channels has a diameter of about 10 Å in both compounds.

To the best of our knowledge the supramolecular assembly described herein is novel in the case of oxamide oxime and *vic*-dioxime metal complexes. The crystal packing generally encountered is a stacking of the molecules either through weak metal-metal intermolecular bonds or intermolecular hydrogen bonds.[13,14] Whether the hexyl chains cooperate in the formation of these structures, or simply fill the empty space, is still unclear. None of the previous reported structures of unsubstituted oxamide oxime exhibits such assemblies.[14] Moreover, it can be noticed that the structure is in some respects reminiscent of a micellization process. Work is underway in our laboratory to determine both the influence of the metal ion and the range of lengths of the alkyl chains that may accommodate such structures. This should provide more information concerning their relative contributions to the building of these structures.

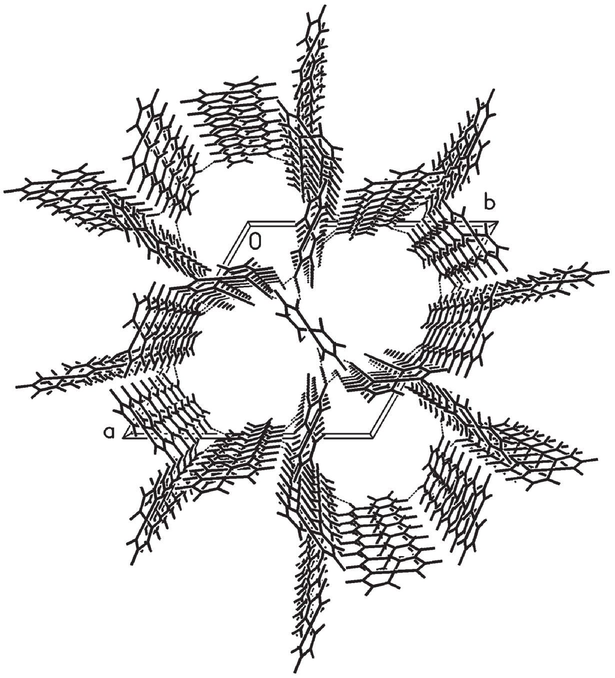

Fig. 3 View showing the tubular channels developing along the *c* axis direction. The carbon atoms of the hexyl chains and hydrogen atoms are omitted for clarity.

Experimental

Synthesis of the ligand (H_2L)

Hexylamine (1 g, 9.88 mmol) was dissolved in absolute ethanol (5 ml) under argon. To this solution (*E*,*E*)-dichloroglyoxime (0.388 g, 2.47 mmol) in absolute ethanol (10 ml) was added dropwise. The mixture was stirred at room temperature overnight. Water was added dropwise until a white precipitate formed. It was filtered, washed with water and then dried. The ligand is soluble in dichloromethane, *n*-hexane, ethanol, acetone and DMF. Yield: 0.400 g (57%), m.p.150 °C. Anal. calcd for $C_{14}H_{30}N_4O_2$: C, 58.70; H, 10.55; N, 19.54; found: C, 59.00; H, 11.61; N, 20.00; IR (ν_{max}/cm^{-1}): 3400 (NH), 3300 (OH), 2920 and 2850 (CH_2), 1650 (C=N), 900 (N–O); δ_H ($CDCl_3$): 8.44 (s, 2H, NOH, disappeared upon D_2O), 5.08 (t, 2H, NH, disappeared upon D_2O), 3.09 (q, 4H, N–CH_2), 1.49 (p, 4H, N–CH_2–CH_2), 1.27 (s, 12H, CH_2), 0.86 (t, 6H, CH_3); δ_C ($CDCl_3$): 147.98 (C=N–O), 42.97 (N–CH_2), 31.51 (N–CH_2–CH_2), 30.81 (CH_2), 26.36 (CH_2), 22.55 (CH_2), 13.99 (CH_3). MS (ES-MS) *m*/*z*: 287 (100) $[M+1]^+$.

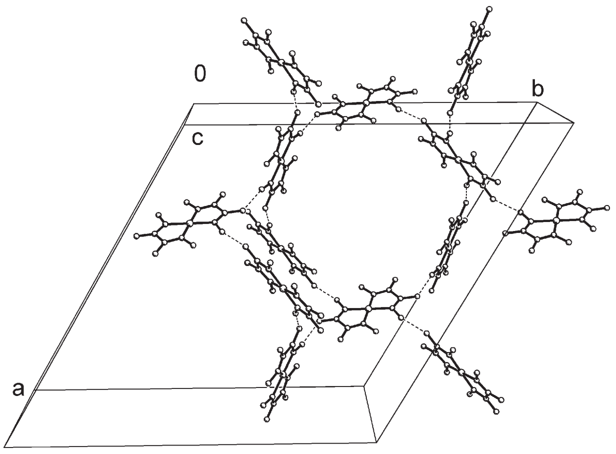

Fig. 2 View of the connectivity between the complexes molecules involving hydrogen bonds between the oximic oxygen atoms (O1) and the amino nitrogen atoms (N3) of the hexamine substituant. The carbon atoms of the hexyl chains and the hydrogen atoms are omitted for clarity. Selected intermolecular distances (Å): O1–N3b, 2.866 (3); O1–N4b, 2.991(3) for **1** and O1–N3b, 2.858(5); O1–N4b, 2.922(5) for **2**. Symmetry code b: $1/3-x+y$, $2/3-x$, $-1/3+z$.

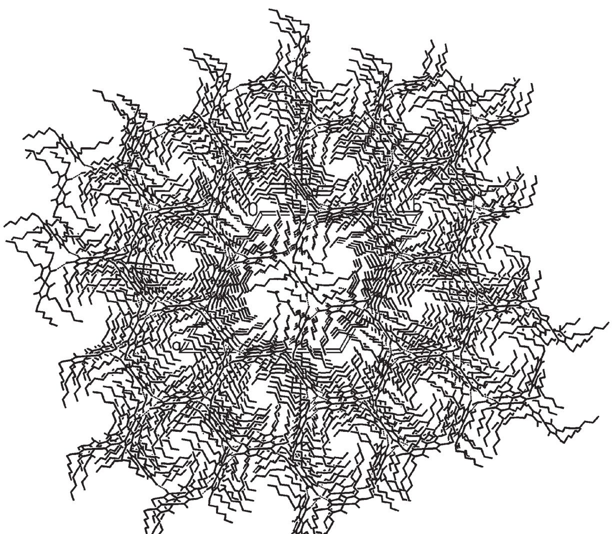

Fig. 4 View along the *c* axis direction with the hexyl chain partially filling the channels. The hydrogen atoms are omitted for clarity.

Synthesis of *N*,*N*′-coordinated complexes [M(HL)$_2$, M = Ni(II), Pd(II)]

To an ethanol solution (5 ml) of H_2L (0.100 g, 0.35 mmol) was added an ethanol solution (2 ml) of the appropiate metal salt [$NiCl_2 \cdot 6H_2O$ (0.041 g, 0.175 mmol) or Na_2PdCl_4 (0.050 g, 0.172 mmol; 8.3 ml, 2.08×10^{-2} mol dm^{-3})] with stirring at 50 °C for 15 min. A distinct change in color and a decrease in the pH value of the solution was observed. Potassium hydroxide (0.017 g, 0.3 mmol) in ethanol (6 ml) was then added and precipitation occurred, leading to red (*E*,*E*)-Ni(HL)$_2$ or yellow (*E*,*E*)-Pd(HL)$_2$ precipitates. The reaction mixture was cooled to room temperature. The red and yellow products were precipitated at 0 °C and filtered off, washed with water and cold ethanol and dried *in vacuo*. Single crystals of the compounds were grown by slow evaporation from ethanol. They are soluble in common organic solvents such as ethanol, dichloromethane, diethyl ether and acetone.

Ni(HL)$_2$. Yield: 0.050 g (45%); m.p. 135 °C. Anal. calcd for $C_{28}H_{58}N_8NiO_4$: C, 53.42; H, 9.29; N, 17.80; found: C, 53.12; H, 9.70; N, 17.40; IR (ν_{max}/cm^{-1}): 3350 (NH), 3130 (OH), 2980 and 2920 (CH_2), 1600 (C=N), 1460, 1320 and 1060 (N–O); δ_H ($CDCl_3$): 16.4 (s, 2H, O–H–O, disappeared upon D_2O), 4.80 (t, 4H, NH, disappeared upon D_2O), 3.20 (q, 8H, N–CH_2), 1.46 (q, 8H, N–CH_2–CH_2), 1.27 (s, 24H, CH_2), 0.88 (t, 12H, CH_3); δ_C ($CDCl_3$):147.38 (C=N–O), 45.27 (N–CH_2), 31.40 (N–CH_2–CH_2), 26.19 (CH_2), 22.49 (CH_2) and 13.97 (CH_3); MS (ES-MS) *m*/*z*: 629 (100) $[M+1]^+$.

Pd(HL)$_2$. Yield: 0.080 g (68%); m.p. 153 °C. Anal. calcd for $C_{28}H_{58}N_8O_4Pd$: C, 49.66; H, 8.63; N, 16.55; found: C, 49.00; H, 8.97; N, 16.06; IR (ν_{max}/cm^{-1}): 3340 (NH), 3140 (OH), 2980 and 2920 (CH_2), 1580 (C=N), 1460, 1320 and 1060 (N–O); δ_H ($CDCl_3$): 6.20 (t, 4H, NH, disappeared upon D_2O), 3.20 (q, 8H, N–CH_2), 1.46 (p, 8H, N–CH_2–CH_2), 1.27 (s, 24H, CH_2), 0.88 (t, 12H, CH_3); δ_C ($CDCl_3$): 143.51 (C=N–O), 40.44 (N–CH_2), 38.91 (N–CH_2–CH_2), 26.19 (CH_2), 21.24 (CH_2) and 8.71 (CH_3); MS (ES-MS) *m*/*z*: 676 (100) $[M+1]^+$.

X-Ray crystallograpy

X-Ray single-crystal diffraction data for compounds **1** and **2** were collected at room temperature (298 K) with a Bruker SMART CCD diffractometer. Both compounds crystallized in the hexagonal $R\bar{3}$ space group (No. 148) and were refined with the hexagonal axes.†

Data for compound 1. $C_{28}H_{58}N_8NiO_4$, FW = 629.5, $a = 27.396(2)$, $b = 12.667(1)$ Å, $U = 8233.6(9)$ Å^3, $Z = 9$, $\rho_{calcd} = 1.143$ g cm^{-3}, $\mu(Mo) = 0.570$ mm^{-1}. Least-squares refinement based on 4275 independent reflections and 187 parameters ($R_{int} = 0.0326$), $R(F) = 0.0534$ [$I > 2\sigma(I)$], $wR(F^2) = 0.1702$ (all data) and GOF = 1.006.

Data for compound 2. $C_{28}H_{58}N_8O_4Pd$, FW = 677.2, $a = 27.874(2)$, $b = 12.410(1)$ Å, $U = 8350(1)$ Å^3, $Z = 9$, $\rho_{calcd} = 1.212$ g cm^{-3}, $\mu(Mo) = 0.539$ mm^{-1}. Least-squares refinement based on 4622 independent reflections and 187 parameters ($R_{int} = 0.0652$), $R(F) = 0.0460$ [$I > 2\sigma(I)$], $wR(F^2) = 0.1504$ (all data) and GOF = 0.651.

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† CCDC reference numbers 199677 and 199678. See http://www.rsc.org/suppdata/nj/b3/b307783g/ for crystallographic data in .cif or other electronic format.