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Alkyl-substituted oxamide oximes and their metal complexes

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ABSTRACT

Nickel(II) and palladium(II) complexes of oxamide oximes substituted with alkyl chains of different length (C_nH_{2n+1}, n = 4, 6, 8, 10, 12 and 16) have been synthesized from the reaction of (*E*,*E*)-monochloroglyoxime with the corresponding amine derivatives. The Ni(II) and Pd(II) complexes have been prepared by reacting the ligand with either $NiCl_2{\cdot}6H_2O$ or Na_2PdCl_4 in ethanol. All the compounds were characterized by elemental analyses, ^{1}H NMR, IR and mass spectra. The molecular structure of bis[(*N*-hexylaminoglyoxime)]palladium(II) (**2b**) was obtained by single crystal X-ray diffraction and it was found to be centrosymmetric at the metal center, which is bound by the four oximic nitrogen atoms of two ligands in a square planar environment. The role of the H-bonding in the structures of these complexes was investigated.

1. Introduction

Research on metal–organic supramolecular chemistry has rapidly developed to produce new materials with interesting structural properties and potential applications in many areas, such as molecular adsorption, ion exchange, heterogeneous catalysis, magnetism and photonic antenna [1–5]. The synthesis and characterization of coordination networks is one of the most active branches of metal–organic supramolecular chemistry. By the self-assembly of well-designed organic ligands and metal ions under appropriate conditions, a variety of novel metallosupramolecular architectures have been achieved so far [1–11].

Hydrogen-bonding interactions have been widely used as one of the principal means to control such molecular assemblies during crystallization and thereby to engineer the structures of crystals [12–15]. However, the synthesis of such functional porous networks is often unsuccessful because of the formation of an interpenetrating structure, which provides only small-size channels or none at all [16–21]. Another reason could be the deformation of the channel structure on the removal of included guest molecules.

In our previous papers, we discovered that nickel(II) and palladium(II) complexes of soluble alkyl (C_4–C_8) substituted oxamide oximes self-assemble through hydrogen bonds to afford metal–organic open frameworks with tubular channels [9,10] (Fig. 1) and we undertaken conformational analyses of the complexes in order to understand the role of the chain lengths and of the metal center in the formation of the tubular channels. The results showed that the formation of infinite tubular channels of alkyl-substituted oxamide oxime Ni(II) and Pd(II) complexes is related to the orientation of the alkyl chains compared to the central core. The best organized channels have been obtained from the Ni(II) and Pd(II) complexes of *N*,*N*′-bis(hexylamino)glyoxime [10] (Fig. 1). In this paper, the nickel(II) and palladium(II) complexes of oxamide oximes substituted with alkyl chains of different lengths (C_nH_{2n+1}, n = 4, 6, 8, 10, 12 and 16) have been synthesized from the reaction of (*E*,*E*)-monochloroglyoxime with the corresponding amine derivatives, and an analysis of their conformations has been carried out.

2. Experimental

2.1. Measurements

Elemental analyses were obtained from a Thermo Finnigan Flash 1112 Instrument. Infrared spectra were recorded on a Perkin Elmer FT-IR System Spectrum BX. ^{1}H NMR spectra were recorded in DMSO-d_6 on a Varian 500 MHz spectrometer. The mass spectra were acquired on a Bruker Daltonics (Bremen, Germany) MicrOTOF mass spectrometer equipped with an electrospray ionization (ESI) source. The instrument was operated in the positive ion mode using a *m/z* range of 50–3000. The capillary voltage of the ion source was set at 6000 V and the capillary exit at 190 V. The nebulizer gas flow was 1 bar and the drying gas flow 8 mL/min.

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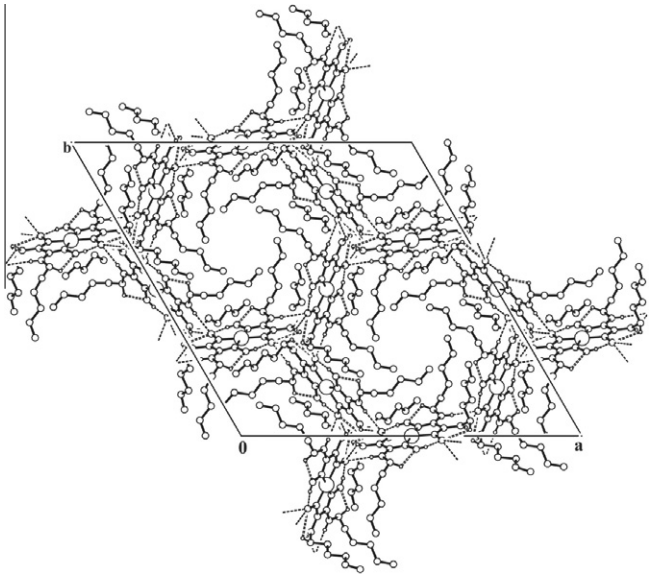

Fig. 1. View of the channel formation of the dihexylaminoglyoxime Ni(II) complex [9,10]. Hydrogen atoms are omitted for clarity.

Table 1
Crystal data and refinement parameters for **2b**.

	2b
Empirical formula	$C_{16}H_{32}N_6O_4Pd$
Formula weight	478.88
T (K)	296(2)
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	7.91540(10)
b (Å)	8.67420(10)
c (Å)	15.2166(2)
α (°)	102.9350(10)
β (°)	92.7020(10)
γ (°)	93.1820(10)
V (Å^3)	1014.78(2)
Z	2
μ (mm^{-1}) (MoKα)	0.948
Reflection collected	15243
Independent reflection	3597
Data/restraints/parameters	3077/4/261
R_{int} (merging R value)	0.0351
θ_{max} (°)	25.03
T_{min}/T_{max}	0.86/0.93
Goodness-of-fit (GOF) on F^2	1.060
R [$F^2 > 2\sigma(F^2)$]	0.0195
wR [all reflections]	0.0550

2.2. Crystallography

Crystallographic data was collected on a Bruker SMART APEX II diffractometer using MoKα radiation (λ = 0.71073 Å). Absorption corrections by multi-scan have been applied to all datasets [22]. The structure was solved by direct methods and refined by full-matrix least squares against F^2 using all data [23]. All non-H atoms were refined anisotropically. H atoms were generally fixed in idealized positions (with the exception of N–H and O–H protons, whose positions were determined from a difference map) with their displacement parameters riding on the values of their parent atoms. The general-purpose crystallographic tool PLATON [24] was used for the structure analysis and presentation of the results. The figures were drawn with DIAMOND (Version 3.1) [25]. The crystal structure and refinement data of all compounds are summarized in Table 1.

2.3. Synthesis

(*E*,*E*)-Monochloroglyoxime was prepared according to a described procedure [26]. All reagents and solvents were reagent-grade quality and they were obtained from commercial suppliers and purified as described in Perrin and Armarego [27].

2.3.1. Synthesis of the ligands (H_2L)

(*E*,*E*)-Monochloroglyoxime (40 mmol) was dissolved in 40 mL of absolute ethanol and was added drop-wise to a solution of the corresponding amine derivative (80 mmol) in 80 mL of absolute ethanol. The mixture was stirred overnight. Water was added dropwise until a white precipitate formed. It was filtered off, washed with water and then dried. The ligands are soluble in dichloromethane, *n*-hexane, ethanol and DMF.

2.3.1.1. Ligand **1**. Yield: 58%; m.p.: 116 °C. *Anal.* Calc. for $C_6H_{13}N_3O_2$: C, 45.27; H, 8.23; N, 26.40. Found: C, 45.34; H, 8.11; N, 26.34%. IR (ν_{max}/cm^{-1}): 3402 (NH), 3220 (OH), 3064 (CH), 2954–2872 (CH_2), 1640 (C=N), 1484, 945 (N–O); ^{1}H NMR (DMSO-d_6) δ (ppm): 11.36 (s, 1H, NOH, disappeared upon addition of D_2O), 10.19 (s, 1H, NOH, disappeared upon addition of D_2O), 7.30 (s, 1H, CH), 5.43 (b, 1H, NH, disappeared upon addition of D_2O), 3.36 (t, 2H, N–*CH*$_2$), 1.40 (m, 2H, N–CH$_2$–*CH*$_2$), 1.25 (m, 2H, CH_2), 0.86 (t, 3H, CH_3); (ESI) *m/z*: 160 [M+H]$^+$.

2.3.1.2. Ligand **2**. Yield: 50%; m.p.: 124 °C. *Anal.* Calc. for $C_8H_{17}N_3O_2$: C, 51.32; H, 9.15; N, 22.44. Found: C, 51.29; H, 9.13; N, 22.34%. IR (ν_{max}/cm^{-1}): 3400 (NH), 3225 (OH), 3050 (CH), 2920–2850 (CH_2), 1650 (C=N), 1460, 940 (N–O); ^{1}H NMR (DMSO-d_6) δ ppm: 11.34 (s, 1H, NOH, disappeared upon addition of D_2O), 10.17 (s, 1H, NOH, disappeared upon addition of D_2O), 7.30 (s, 1H, CH), 5.43 (t, 1H, NH, disappeared upon addition of D_2O), 3.36 (t, 2H, N–*CH*$_2$), 1.40 (p, 2H, N–CH$_2$–*CH*$_2$), 1.25 (m, 6H, CH_2), 0.85 (t, 3H, CH_3); (ESI) *m/z*: 188 [M+H]$^+$.

2.3.1.3. Ligand **3**. Yield: 60%; m.p.: 138 °C. *Anal.* Calc. for $C_{10}H_{21}N_3O_2$: C, 55.79; H, 9.83; N, 19.52. Found: C, 55.63; H, 9.80; N, 19.40. IR (ν_{max}/cm^{-1}): 3405 (NH), 3250 (OH), 3050 (CH), 2925–2850 (CH_2), 1643 (C=N), 1480, 935 (N–O); ^{1}H NMR (DMSO-d_6) δ ppm: 11.35 (s, 1H, NOH, disappeared upon addition of D_2O), 10.19 (s, 1H, NOH, disappeared upon addition of D_2O), 7.30 (s, 1H, CH), 5.43 (b, 1H, NH, disappeared upon addition of D_2O), 3.36 (t, 2H, N–*CH*$_2$), 1.39 (m, 2H, N–CH$_2$–*CH*$_2$), 1.24 (m, 10H, CH_2), 0.86 (t, 3H, CH_3); (ESI) *m/z*: 216 [M+H]$^+$.

2.3.1.4. Ligand **4**. Yield: 56%; m.p.: 145 °C. *Anal.* Calc. for $C_{12}H_{25}N_3O_2$: C, 59.28; H, 10.28; N, 17.27. Found: C, 59.00; H, 10.19; N, 17.21%. IR (ν_{max}/cm^{-1}): 3400 (NH), 3200 (OH), 3040 (CH), 2900–2850 (CH_2), 1650 (C=N), 1460, 940 (N–O); ^{1}H NMR (DMSO-d_6) δ ppm: 11.34 (s, 1H, NOH, disappeared upon addition of D_2O), 10.16 (s, 1H, NOH, disappeared upon addition of D_2O), 7.30 (s, 1H, CH), 5.40 (t, 1H, NH, disappeared upon addition of D_2O), 3.37 (t, 2H, N–*CH*$_2$), 1.40 (m, 2H, N–CH$_2$–*CH*$_2$), 1.23 (m, 14H, CH_2), 0.88 (t, 3H, CH_3); (ESI) *m/z*: 244 [M+H]$^+$.

2.3.1.5. Ligand **5**. Yield: 60%; m.p.: 161 °C. *Anal.* Calc. for $C_{14}H_{29}N_3O_2$: C, 61.96; H, 10.77; N, 15.48. Found: C, 62.00; H, 11.00; N, 15.18%. IR (ν_{max}/cm^{-1}): 3400 (NH), 3240 (OH), 3060 (CH), 2900–2850 (CH_2), 1640 (C=N), 1460, 954 (N–O); ^{1}H NMR (DMSO-d_6) δ ppm: 11.35 (s, 1H, NOH, disappeared upon addition of D_2O), 10.18 (s, 1H, NOH, disappeared upon addition of D_2O), 7.30 (s, 1H, CH), 5.43 (t, 1H, NH, disappeared upon addition of