A Novel Nickel(II) Complex Adopting a *cis*-Configuration: Solvothermal Synthesis and Crystal Structure of $[NiL_2(H_2O)_4]$ (L = 1,4-Dihydropyrazine-2,3-dione-5,6-dicarboxylate)

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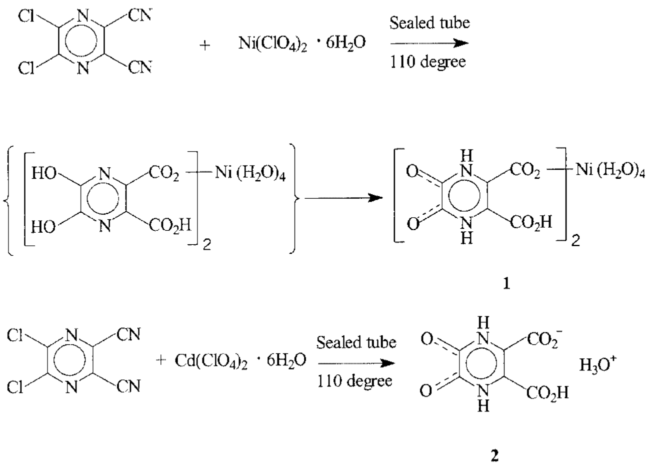
Under solvothermal reaction conditions, the reaction of 5,6-dichloropyrazine-2,3-dicarbonitrile and $[Ni(ClO_4)_2]{\cdot}6H_2O$ produces a novel *cis*-nickel(II) complex $[NiL_2(H_2O)_4]$ (**1**) (L = 1,4-dihydropyrazine-2,3-dione-5,6-dicarboxylate), whereas only hydrated 1,4-dihydropyrazine-2,3-dione-5,6-dicarboxylic acid (**2**) was obtained as a single phase when $[Cd(ClO_4)_2]{\cdot}6H_2O$ was used instead of $[Ni(ClO_4)_2]{\cdot}6H_2O$.

Introduction

Recently, the use of hydro(solvo)thermal techniques for synthesizing coordination compounds with interesting optical and/or magnetic properties has attracted increasing interest.[1,2] Most examples focus on high-dimensional coordination polymers, and the hydrolysis of substituted cyano, ester or aldehyde groups into a carboxylate group has often been used as the key step in designing such functionalized coordination polymers. However, rare examples have involved the hydrolysis of other substituted groups under hydro(solvo)thermal conditions. Here we present the hydro(solvo)thermal synthesis and crystal structure of a novel nickel(II) complex $[NiL_2(H_2O)_4]$ (**1**) (L = 1,4-dihydropyrazine-2,3-dione-5,6-dicarboxylate), which adopts an unusual *cis*-configuration. Interestingly, no cadmium complex could be isolated from the reaction when $[Cd(ClO_4)_2]{\cdot}6H_2O$ was used instead of $[Ni(ClO_4)_2]{\cdot}6H_2O$ under the same solvothermal conditions: only hydrated 1,4-dihydropyrazine-2,3-dione-5,6-dicarboxylic acid (**2**) was formed. The cyano groups of the reactant 5,6-dichloropyrazine-2,3-dicarbonitrile were found to have been hydrolyzed into carboxylate groups and the chloro groups into hydroxyl groups (there is an autoisomerization from the enol form into the ketone form) during the hydro(solvo)thermal reaction in both cases (Scheme 1).



Scheme 1

Results and Discussion

Green crystals of **1** were obtained by treating 5,6-dichloropyrazine-2,3-dicarbonitrile and $[Ni(ClO_4)_2]{\cdot}6H_2O$ under solvothermal conditions. Two strong peaks at $\tilde{\nu}$ = 1688 and 1555 cm^{-1} in the IR spectrum of complex **1** could be assigned to the antisymmetric C=O stretching vibrations of uncoordinated and coordinated carboxylate groups, respectively. The absence of characteristic peaks for cyano groups in the region of 2200 cm^{-1} indicates the formation of carboxylate groups by the hydrolysis of the precursor ligand.[1c] Two strong and sharp peaks around $\tilde{\nu}$ = 3551 and 3448 cm^{-1} indicate the presence of coordinated water

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molecules.[3] The strong and sharp peak at $\tilde{\nu} = 3373\ \mathrm{cm}^{-1}$ is assigned to the N−H stretching mode of ammonium while the broad strong band around $\tilde{\nu} = 3116\ \mathrm{cm}^{-1}$ can be assigned to the O−H stretching mode of a protonated carboxylate group. A TGA study shows that **1** is thermally stable to about 155 °C and decomposes with the loss of four molecules of water and two molecules of CO_2 over the temperature range 155−290 °C; this also indicates that all four water molecules are coordinated to metal center.[4]

As shown in Figure 1, the crystal structure of **1** consists of isolated 1,4-dihydropyrazine-2,3-dione-5,6-dicarboxylatonickel(II) tetrahydrate molecules $[NiL_2(H_2O)_4]$, where the two 1,4-dihydropyrazine-2,3-dione-5,6-dicarboxylate ligands adopt an unusual *cis*-configuration. To the best of our knowledge, this is the first mononuclear *cis* complex of carboxylate-substituted pyrazine derivatives, although the *cis*-configuration is quite normal for molybdenum complexes of 3,6-di-*tert*-butylcatechol,[5] and the two-dimensional copper complex $[Cu_2(pzdc)_2(pyz)]_n$ (pzdc = pyrazine-2,3-dicarboxylate, pyz = pyrazine) also exhibits such a *cis*-coordination.[6a] This coordination mode is quite similar to that in $[Co^{II}\{OOC(CH_2)_{10}COO\}]\cdot 2H_2O$,[7] where each cobalt atom is coordinated by three carboxylate groups from three *n*-dodecane-α,ω-dioate ligands from one side and two water molecules, in a *cis*-orientation. Generally, there is a chelating interaction involving the nitrogen atom and the oxygen atom of adjacent deprotonated carboxylate ligands in complexes of singly and doubly deprotonated 2,3-pyrazinedicarboxylic acid ($pyzdcH_2$).[4,6] However, the hydrogen atoms bonded to the nitrogen atoms of the pyrazine rings in complex **1** prevent the formation of such a chelate.

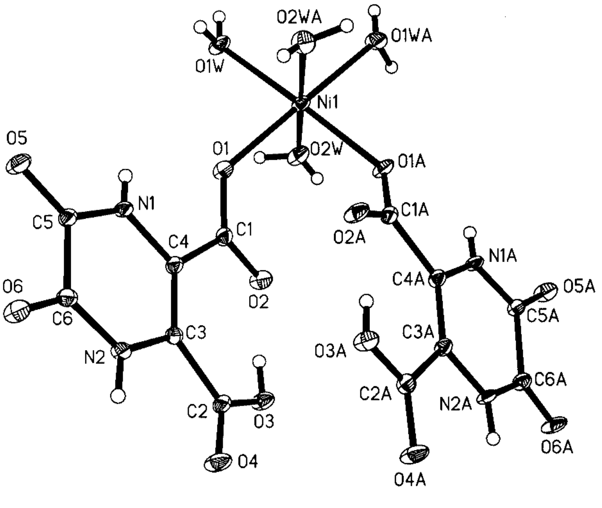

Figure 1. ORTEP drawing of complex **1** with labeling scheme and thermal ellipsoids at the 50% probability level for C, N and O atoms; the spheres of the hydrogen atoms have been arbitrarily reduced; selected bond lengths (Å) and angles (°): Ni(1)−O(1w) 2.041(3), Ni(1)−O(1) 2.046(2), Ni(1)−O(2w) 2.059(3); O(1)−Ni(1)−O(1w) 84.86(10), O(1)−Ni(1)−O(1a) 93.94(13)

The nickel atom has a distorted octahedral environment. It is coordinated by four water molecules and two oxygen atom from the carboxylate groups of two 1,4-dihydropyrazine-2,3-dione-5,6-dicarboxylate ligands, which are found in a *cis*-orientation. The uncoordinated carboxylate groups of the 1,4-dihydropyrazine-2,3-dione-5,6-dicarboxylate ligands are still protonated. The O2···O3 distance of 2.412 Å indicates that there is no intramolecular hydrogen bond involving the carboxylate hydrogen and O2. This is quite different from complexes of singly deprotonated 2,3-pyrazinedicarboxylic acid $[Co\{pz(COO)COOH\}_2(H_2O)_2]$[6b] and $[Ni(pyzdcH)_2(H_2O)_2]$,[4] both of which show a *trans*-configuration, a chelate interaction and a strong intramolecular hydrogen bond between the carboxylate hydrogen and the nearest oxygen atom of the deprotonated carboxylate group. The $Ni-O_{carboxylate}$ bond length [2.046(2) Å] is a little longer than that in $[Ni(pyzdcH)_2(H_2O)_2]$ [2.021(1) Å],[4] whereas the Ni−Ow bond lengths [average 2.050(3) Å] are a little shorter than those in $[Ni(pyzdcH)_2(H_2O)_2]$ [2.091(1) Å].[4] The C5−O5 and C6−O6 bond lengths [1.234(3) and 1.227(3) Å, respectively] are shorter than those of C−O single bonds, indicating that the 1,4-dihydropyrazine-2,3-dione-5,6-dicarboxylate ligands are present as their ketone tautomers.

The intermolecular hydrogen bonds play an important role in the stabilization of the structure of **1**. As shown in Figure 2, there are extensive hydrogen bonds between coordinated water molecules and uncoordinated carboxylate groups ($Ow\cdots O_{carboxylate}$ = 2.774 Å), coordinated water molecules and dione groups ($Ow\cdots O_{dione}$ = 2.885Å), uncoordinated carboxylate groups and dione groups ($O_{dione}\cdots O_{carboxylate}$ = 2.862 Å), and also between dione groups and the nitrogen atoms of the pyrazine rings ($O_{dione}\cdots N$ = 2.887 or 2.954 Å) from neighboring molecules. Consequently, a two-dimensional supramolecular structure is formed.

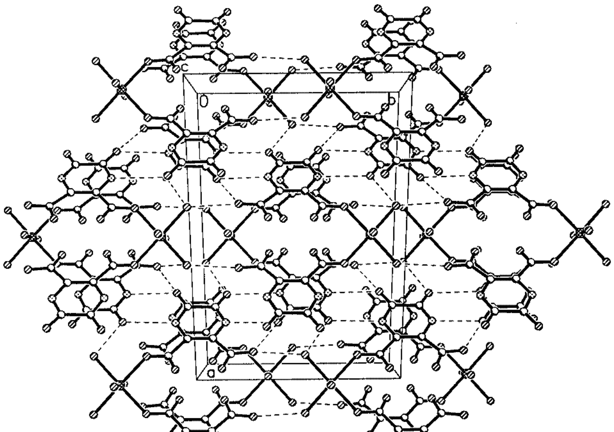

Figure 2. Projection down the *c*-axis of complex **1**

Only one carboxylate group of compound **2** is deprotonated. The hydrogen atom position indicates the two carboxylate groups in compound **2** share a single proton (Figure 3); a similar trend has also been observed in the complex [Co{pz(COO)COOH}$_2$(H$_2$O)$_2$].[6b] The other proton is combined with a water molecule to form the cation H_3O^+. The crystal structure of **2** is therefore composed of discrete H_3O^+ cations and singly deprotonated 1,4-dihydropyrazine-2,3-dione-5,6-dicarboxylate anions. The C1−O3 bond length [1.214(2) Å] is a little smaller than the $C-O_{dione}$ bond lengths in the 1,4-dihydropyrazine-2,3-dione-5,6-dicarboxylate ligands of **1** [the C5−O5 and C6−O6 bond lengths are1.234(3) and 1.227(3) Å, respectively]. There are extensive hydrogen bonds between protonated water molecules and the oxygen atoms of the dione groups ($Ow\cdots O_{dione}$ = 2.879 Å) and also the carboxylate groups from neighboring singly deprotonated 1,4-dihydropyrazine-2,3-dione-5,6-dicarboxylate anions ($Ow\cdots O_{carboxylate}$ = 2.874 Å). These hydrogen bonding interactions force the structure into an interesting two-dimensional layered supramolecular array, as shown in Figure 4.

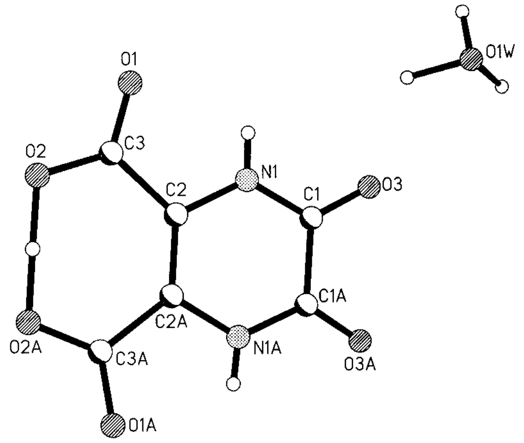

Figure 3. ORTEP drawing of complex **2** showing 50% probability displacement ellipsoids and the atom numbering scheme

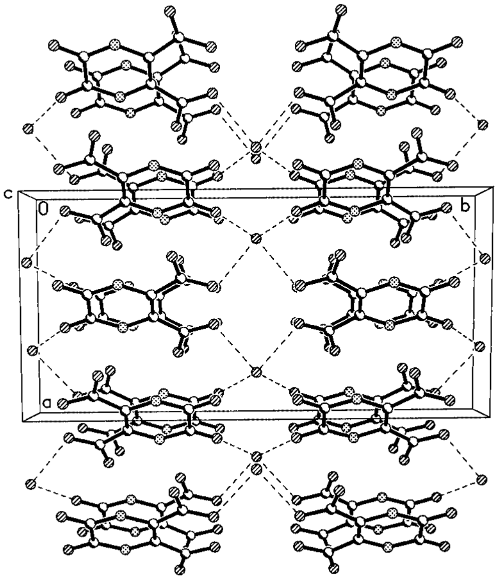

Figure 4. Projection down the *c*-axis of complex **2**

In conclusion, this study illustrates that chloro groups can also undergo a hydrolysis reaction under hydro(solvo)-thermal conditions. This new reaction could be useful for designing structures with a novel topology. Furthermore, such a reaction may also find potential applications in organic synthesis. More investigations are currently underway.

Experimental Section

Synthesis of 1: 5,6-Dichloropyrazine-2,3-dicarbonitrile (80 mg, 0.4 mmol) and [Ni(ClO$_4$)$_2$]·6H$_2$O (73 mg, 0.2 mmol) were placed in a thick Pyrex tube (ca. 20 cm long). After addition of 0.2 mL of water and 0.8 mL of ethanol, the tube was frozen with liquid N_2, evacuated under vacuum and sealed with a torch. The tube was then heated at 110 °C for three days to give pure green rod-shaped crystals of **1** in 60% yield (63 mg) based on 5,6-dichloropyrazine-2,3-dicarbonitrile. Compound **1** is insoluble in common organic solvents. $C_{12}H_{14}N_4NiO_{16}$ (529.0): calcd. C 27.25, H 2.67, N 10.59; found C 27.12, H 2.81, N 10.47. IR (KBr): $\tilde{\nu}$ = 3551(s), 3448(s), 3373(s), 3116(s), 1688(vs), 1555(s), 1459(s), 1370(s), 1250(w), 1159(m), 1103(m), 889(m), 805(w), 767(m), 702(w), 500(w), 464(m) cm^{-1}.

Synthesis of 2: This compound was prepared as brown tablet-shaped crystals from 5,6-dichloropyrazine-2,3-dicarbonitrile and [Cd(ClO$_4$)$_2$]·6H$_2$O by the procedure described above for **1**. Yield: 65 mg (75%). $C_{12}H_{12}N_4O_{14}$ (436.2): calcd. C 66.08, H 5.55, N 25.69; found C 65.94, H 5.62, N 25.39%. IR (KBr): $\tilde{\nu}$ = 3444(b, m), 3204(vs), 1718(vs), 1587(s), 1497(s), 1434(vs), 1367(s), 1233(m), 1150(w), 1095(w), 981(w), 857(m), 798(w), 771(w), 709(w), 669(m), 589(w), 461(w) cm^{-1}.

Caution: *Ni(ClO$_4$)$_2$·6H$_2$O and Cd(ClO$_4$)$_2$·6H$_2$O are potentially explosive and should be handled with care!*

X-ray Crystal Structure Determination: Crystal data collection was carried out using a Rigaku RAXIS RAPID IP imaging plate system with Mo-K_α radiation (λ = 0.71073Å). The data were corrected for Lorentz-polarization effects, and absorption corrections were applied. The structure was solved by direct methods and refined by a full-matrix least-squares technique based on F^2 using the SHELXL-97 program.[8] All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were located in difference Fourier maps.

Crystal Data For 1: $C_{12}H_{14}N_4NiO_{16}$, monoclinic, space group *C2/c*, *Mr* = 528.98, *a* = 17.858(4), *b* = 11.098 (2), *c* = 9.869(2) Å, β = 119.87(3)°, *V* = 1696.1(6) Å^3, *Z* = 4, *Dc* = 2.072 g·cm^{-3}, *T* = 293(2)K, μ = 1.254 mm^{-1}, R_1 = 0.0441, wR_2 = 0.0875 for 1356 observed reflections [$I > 2\sigma(I)$] from 1927 independent reflections, GOF = 0.962.

Crystal Data For 2: $C_{12}H_{12}N_4O_{14}$, monoclinic, space group *C2/m*, *Mr* = 218.13, *a* = 8.8928(18), *b* = 18.176(4), *c* = 5.0350 (10) Å, β = 96.65(3)°, *V* = 808.4(3) Å^3, *Z* = 4, *Dc* = 1.792 g·cm^{-3}, *T* = 293(2)K, μ = 0.168 mm^{-1}, R_1 = 0.0510, wR_2 = 0.1587 for 848 observed reflections [$I > 2\sigma(I)$] from 954 independent reflections, GOF = 1.083.

CCDC-178134 (**1**) and CCDC-178135 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union

Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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