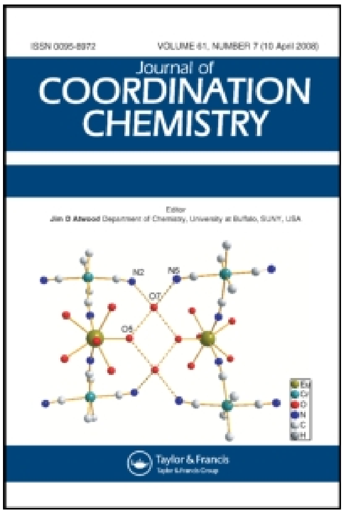

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The first crystal structure with pyrazine-2-carboxylato-3-amide as a ligand. Synthesis and structure of <i>cis</i>-<i>N</i>, <i>cis</i>-<i>O</i>, <i>trans</i>-<i>O</i>-diaquobis(pyrazine-2-carboxylato- 3-amide)nickel dihydrate

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The first crystal structure with pyrazine-2-carboxylato-3-amide as a ligand. Synthesis and structure of *cis-N*, *cis-O*, *trans-O*-diaquobis(pyrazine-2-carboxylato-3-amide)nickel dihydrate

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The first structural example of a metal complex containing the ligand pyrazine-2-carboxylato-3-amide is presented. The ligand is most likely generated via hydrolysis of 2,3-pyrazine dicarboxyamide, and the Ni complex can be considered as a model of a potential intermediate for a general amide hydrolysis catalysis. The observed non-centrosymmetric structure, including *cis*-coordinated water molecules, is rare for complexes containing pyridine-2-carboxylato- or pyrazine-2-carboxylato-based ligands. A classical $R_2^2(8)$ hydrogen-bonding motif involving the non-coordinated amide groups of neighboring molecules generates one-dimensional zig-zag tapes and a nearly perpendicular twist of the amide group out of the pyrazine plane. Further hydrogen bonding via free and coordinated water molecules links the tapes in three dimensions.

Keywords: Structure; Hydrolysis; Nickel; 2,3-Pyrazine dicarboxyamide

1. Introduction

The area of metal-organic frameworks or coordination polymers has been the subject of an exponential growth in research activity, based on the potential of these materials as adsorbents, catalysts, and other functional materials [1]. The organic linkers integral to the synthesis of these materials are by definition multi-functional so as to coordinate to more than one metal center or cluster. One linker which has received attention recently is 2,3-pyrazine dicarboxylic acid [2]. A related yet essentially unexplored linker is 2,3-pyrazine dicarboxyamide (pzda); there are only a few reports of structurally characterized coordination compounds with pzda as a ligand [3]. A hypothesized advantage of pzda is that coordination through one N atom and the carboxylic O atom would allow the other N atom free to enhance targeted functionalities.

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One result of our efforts in this area is the herein reported crystal structure of *cis-N*, *cis-O*, *trans-O*-diaquobis(pyrazine-2-carboxylato-3-amide)nickel dihydrate **1**, which is to the best of our knowledge the first reported crystal structure in which pyrazine-2-carboxylato-3-amide (L) is coordinated to a metal. A few reports with L or closely related species as ligands have appeared [4], but the structures have only been inferred from spectroscopic, magnetic, and analytical data, leaving the actual coordination geometry for these complexes in doubt. The title complex is a rare example of a compound in this class of molecules with a non-centrosymmetric coordination geometry and *cis* coordinated H_2O molecules.

2. Experimental

$Ni(NO_3)_2 \cdot 6H_2O$ (JT Baker Chemicals) and 2,3-pyrazine dicarboxyamide (Aldrich Chemicals) were used as received. Deionized water was used in the reaction. Elemental analysis was performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. The infrared spectrum was recorded on a Perkin-Elmer System 2000 FT-IR spectrometer.

2.1. *Synthesis*

In a 30 mL glass vial, 2,3-pyrazine dicarboxyamide (0.11 g, 0.68 mmol) was dissolved in H_2O (20 mL) to give a gold-yellow solution. $Ni(NO_3)_2 \cdot 6H_2O$ (0.098 g, 0.37 mmol) was separately dissolved in H_2O (5 mL) to give a pale green solution, and this solution was subsequently added to the pzda solution. The vial containing the resulting dark yellow solution was capped and stored at room temperature. After 3 months, dark blue crystals had formed. The pale yellow supernatant was decanted off, and the crystals were washed with 2 × 25 mL H_2O, 25 mL MeOH, then briefly dried, providing blue-green crystals of **1** (0.13 g, 82% yield, based on pzda). Anal. Calcd for $C_{12}H_{16}N_6NiO_{10}$ (%): C, 31.13; H, 3.48; N, 18.15. Found: C, 30.99; H, 3.49; N, 18.28. IR (KBr, cm^{-1}): 3435, 3271, 3144, 1680, 1652, 1572, 1533, 1464, 1433, 1396, 1354, 1228, 1171, 1121, 1067, 880, 661, 546, 459.

2.2. *X-ray crystallography*

X-ray intensity data were collected using Mo-Kα radiation at room temperature on a Siemens goniometer platform equipped with a Bruker-Nonius Apex II area detector. The data were processed with SAINT software [5] and corrected for absorption with SADABS [6]. Structure solution and parameter refinement were performed using the SHELXTL97 software suite [7]. Molecular geometry calculations were performed with PLATON [8]. The structure was solved by direct methods, and parameters were refined using full-matrix least squares against $|F|^2$. All non-hydrogen atoms were refined allowing for anisotropic displacement. Hydrogen atoms were found from the Fourier difference maps and freely refined.

Table 1. Crystal data, data collection, and refinement parameters for *cis-N*, *cis-O*, *trans-O*-diaquobis(pyrazine-2-carboxylato-3-amide)nickel dihydrate **1**.

Formula	$C_{12}H_{16}N_6NiO_{10}$
Formula wt. ($g\,mol^{-1}$)	463.02
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	16.620(3)
b (Å)	7.0141(11)
c (Å)	15.401(3)
β (°)	102.685(2)
Volume (Å^3)	1751.5(5)
Z	4
D_{Calcd} ($g\,cm^{-3}$)	1.756
T (K)	295
λ (Mo-Kα) (Å)	0.71073
Measured reflections	6935
Independent reflections	1939
R_{int}	0.014
Observed reflections*	1812
μ (mm^{-1})	1.179
Final R	0.0230
Final R_w^2	0.0663
S	1.06

*$I > 2.0\sigma(I)$.

3. Results

The IR data suggest that some sort of inequivalence has arisen in the starting pzda during the synthesis, as evidenced by the two sets of strong bands, one at 1680 and 1652 cm^{-1} corresponding to ν(CO), and the other at 1396 and 1354 cm^{-1}, for ν(COX) (X = N, O). These assignments are consistent with those for metal complexes containing pzda or related ligands such as pyrazine-2,3-dicarboxylic acid [4d, 9]. However, as in the case of the previous studies, the IR data cannot readily distinguish between a monomeric or polymeric structure, the dimensionality of any eventual polymeric structure, nor the exact stereochemical arrangement around the metal center.

An ORTEP [10] of **1** is shown in figure 1; table 2 contains relevant bond distances and angles. The refined structure confirms the partial hydrolysis of the starting pzda. While refinement of protons in the vicinity of transition metals can be problematic, there is no observable electron density near O(2) which could imply that this is actually an N atom from a deprotonated amide. The unit cell parameters for **1** are nearly identical to those determined for a zinc compound of the formula $ZnL_2 \cdot 4H_2O$ [4a], but for which no structural solution has been published. The bond distances for the coordinated carboxylato group and the non-coordinated amide group are consistent with the formulation and compare well with previously reported values [9d, 11].

The Ni center is in a slightly distorted octahedral environment, consisting of two non-centrosymmetrically oriented L and two *cis* water ligands. The Ni atom is located on a two-fold rotation axis and the two halves of the molecule are related by symmetry. Except for the chelate angle N1–Ni–O2 of 80.25(5)° and the angle of 82.11(5)° between the water ligands (O4–Ni–O4*), all unique *cis* angles are between 91 and 96° and the two unique *trans* angles are not less than the 170°. The orientation of the two L's is such

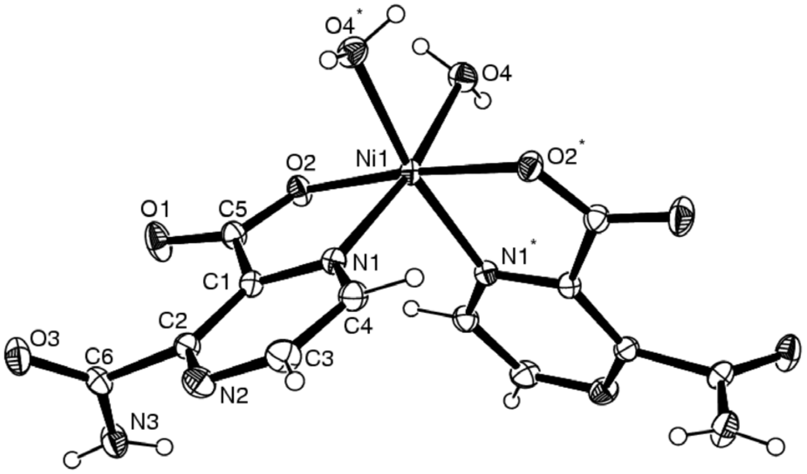

Figure 1. ORTEP of *cis-N*, *cis-O*, *trans-O*-diaquobis(pyrazine-2-carboxylato-3-amide)nickel dihydrate **1** with 30% thermal ellipsoids. The waters of crystallization are not shown.

Table 2. Selected bond distances (Å) and angles (°) for *cis-N*, *cis-O*, *trans-O*-diaquobis(pyrazine-2-carboxylato-3-amide)nickel dihydrate **1**.

Ni1–N1	2.0724(13)
Ni1–O4	2.0751(13)
C5–O2	1.2718(19)
C6–N3	1.312(2)
Ni1–O2	2.0403(11)
C5–O1	1.230(2)
C6–O3	1.235(2)
N1–Ni1–O2	80.25(5)
N1–Ni1–O4	170.32(5)
N1–Ni1–N1*	96.01(5)
O2–Ni1–O4*	91.60(5)
O2–Ni1–O2*	174.21(5)
N1–Ni1–O4*	91.34(5)
N1–Ni1–O2*	95.84(5)
O2–Ni1–O4	92.77(5)
O4–Ni1–O4*	82.11(5)

*Indicates atoms related by symmetry, as indicated in figure 1.

that the coordinated O atoms are *trans*, while the coordinated N atoms are *cis*. The bond distances and angles around the Ni center are consistent with those observed for related complexes, such as Ni(pyridine-2-carboxylato-3-carboxylate)$_2$(H$_2$O)$_2$ [9d], Ni(pyrazine-2-carboxylato-3-carboxylate)$_2$(H$_2$O)$_2$ [11c], and Ni(pyrazine-2-carboxylato-3-amine)$_2$(H$_2$O)$_2$ [11d]. The angle between the pyrazine plane defined by N1, N2, and C1–C4 and the plane containing the non-hydrolyzed amide, as defined by C2, C6, O3, and N3, is 70.9(1)°. The angle between the pyrazine plane and the plane of the coordinated carboxylato group, i.e., C1, C5, O1, and O2 is 11.2(1)°. The angle between the two planar pyrazine rings is 100.5(1)°.

Table 3 provides the geometrical data for the hydrogen bonds found in the structure. The free, non-hydrolyzed amide group forms a classical $R_2^2(8)$ hydrogen-bonding motif

Table 3. Hydrogen bonding parameters in *cis-N*, *cis-O*, *trans-O*-diaquobis(pyrazine-2-carboxylato-3-amide)nickel dihydrate **1**.

Donor–H···Acceptor	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (°)	∠(D–H···A) (°)
N3–H1···O3	0.80(2)	2.13(2)	2.925(2)	172(2)
N3–H2···O5	0.78(3)	2.17(3)	2.946(2)	175.4(18)
O4–H5···O3	0.84(3)	1.91(3)	2.7198(18)	164(3)
O4–H6···O5	0.82(3)	2.05(3)	2.826(2)	159(3)
O5–H7···O2	0.76(3)	2.14(3)	2.848(2)	154(3)
O5–H8···O1	0.76(3)	2.00(3)	2.743(2)	170(3)

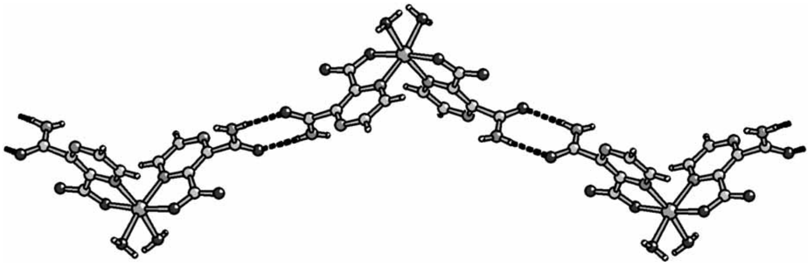

Figure 2. The one-dimensional tapes in *cis-N*, *cis-O*, *trans-O*-diaquobis(pyrazine-2-carboxylato-3-amide)-nickel dihydrate **1** formed via hydrogen bonded amide groups.

with the amide group of a neighboring molecule, forming zig-zag one-dimensional tapes, as shown in figure 2. Further hydrogen bonding via the free and coordinated waters connects these tapes into a three-dimensional hydrogen-bonded structure.

4. Discussion

A comprehensive SciFinder search failed to provide any previous examples of crystal structures containing L. The presence of divalent metal ions Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} enhances amide hydrolysis catalysis, particularly when chelation of the carboxyl oxygen and the heteroaryl N atom in pyridine-based deriviatives to the metal ion is possible [12]; in particular, Ni^{2+} has been shown to catalyze both the OH^- and the H_2O hydrolysis reactions [13]. Hydrolysis of the amide linkage, potentially catalyzed by the added metal salt, is therefore the most likely cause of formation of the carboxylato group. Due to the *N*,*O*-chelation of L, **1** might be considered a model intermediate in this type of hydrolysis catalysis. A few structurally characterized examples involving ligands formed from partially hydrolyzed esters have recently appeared [14].

The *cis-N*, *trans-O* coordination stereochemistry of the two L and the *cis*-coordinated H_2O ligands in **1** are unusual for complexes containing 2-pyridinecarboxylato- or 2-pyrazinecarboxylato-based ligands. Nearly all other related molecules possess all-*trans* stereochemistries [9d, 11]. The only known analogous structure is that of $Mn(2\text{-pyrazinecarboxylato})_2(H_2O)_2$. For this complex, the angle between the coordinated water molecules O(water)–Mn–O(water) is 79.97°, similar to the corresponding angle in **1**, while the angle between the pyrazine planes is considerably larger, 128.43(1)° [11a, b]. Additionally, the structure of this complex is more strongly deformed from an ideal octahedral geometry than that of **1**, with, for example, a chelating N–Mn–O angle equal to 74.60(3)° and the largest *trans* angle equal to 166.51(3)°. The Mn–X bond distances in the complex are also longer than in **1**, in particular the Mn–N bond distance of 2.3071(9) Å. Recently, the structure of a *cis* Ni complex, $NiL'_2(H_2O)_4$ ($L' = $ 1,4-dihydropyrazine-2,3-dione-5,6-dicarboxylate), was reported [15], while the structure of *catena*-poly[[diaquopyridinenickel(II)]-μ-pyridine-2,3-dicarboxylato] has *cis* water ligands, and an overall structural geometry which mimics **1**, i.e., *cis*, *cis*, *trans-N,O,O* [16]. The O(water)–Ni–O(water) angles in these complexes are all considerably larger, 89.04(12), 89.45(11), and 96.40(16), and 90.36(15)°, respectively.

The plane of the non-coordinated amide group is nearly perpendicular to the plane of the pyrazine ring. Generally, in this class of compounds, the geometric relationship of non-chelated carboxyl groups to the parent aromatic ring is guided by one of two possibilities. One is the existence of an intramolecular hydrogen bond between a protonated carboxylic group in the 3-position and the non-coordinated oxygen in the coordinated carboxylato group, resulting in nearly planar geometry throughout the ligand [9d, 11c]. In the other situation, the non-coordinated group is twisted by varying degrees out of the pyrazine plane, due to covalent bonding (for polymeric compounds) [17], ionic bonding to counterions [18], intermolecular hydrogen bonding to a different functional group on an adjacent molecule [3b], intermolecular hydrogen bonding to a water of crystallization [19], van der Waals forces [14a], or combination of these [20]. These distortions need not be large, as evidenced in $[Ni(H_2O)_6][Ni(2,4\text{-pyridinedicarboxylate})_2(H_2O)_2]$, where the comparable angles are 15.5(2)° for the uncoordinated, and 6.4(2)° for the coordinated carboxylato groups, respectively, and are due to interionic hydrogen bonding [11e]. For **1**, the driving force for the large twist of the amide group is most likely the steric demands accompanying the thermodynamically favored formation of the one-dimensional tapes.

Summarizing, the first structural example of a metal complex containing the ligand pyrazine-2-carboxylato-3-amide is presented. This ligand is most likely generated via hydrolysis of 2,3-pyrazine dicarboxyamide. Hydrolysis of pyridine-based amides is known to be catalyzed by nickel salts, particularly when chelation effects can occur; thus complex **1** might be considered a model of a potential intermediate for this general type of hydrolysis catalysis. The structure exhibits the stereochemical motifs of a non-centrosymmetric coordination geometry and *cis*-coordinated water molecules, which are rare for complexes containing pyridine-2-carboxylato- or pyrazine-2-carboxylato-based ligands. Hydrogen bonding between the non-coordinated amide groups of neighboring molecules generates one-dimensional zig-zag tapes and a nearly perpendicular twist of the amide group out of the pyrazine plane. Further hydrogen bonding links the tapes into a three-dimensional hydrogen-bonded structure.

Supplementary material

CCDC 602944 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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