

## X-ray powder structure of a new two-dimensional nickel(II) coordination polymer with pyrazine-2,3,5,6-tetracarboxylic acid

Montserrat Alfonso, Antonia Neels and Helen Stoeckli-Evans\*

Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51,  
CH-2000 Neuchâtel, Switzerland  
Correspondence e-mail: helen.stoeckli-evans@ich.unine.ch

Received 22 December 2000

Accepted 27 June 2001

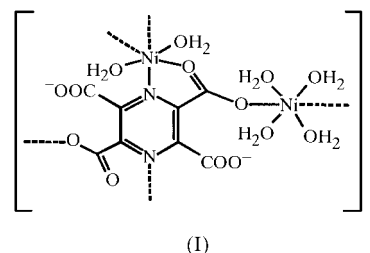
The new nickel(II) coordination polymer poly[*diaqua-nickel(II)-μ-(pyrazine-2,3,5,6-tetracarboxylato)-tetraaqua-nickel(II)*],  $\{[\text{Ni}(\text{C}_8\text{N}_2\text{O}_8)(\text{H}_2\text{O})_2]\text{Ni}(\text{H}_2\text{O})_4\}_n$ , has been synthesized and characterized both spectroscopically and crystallographically, by X-ray powder diffraction analysis. In this two-dimensional coordination polymer,  $\text{Ni}^{\text{II}}$  ions are bridged by pyrazine-2,3,5,6-tetracarboxylic acid, coordinating in a bis-bidentate manner, so forming one-dimensional polymeric chains. The chains are linked by a second  $\text{Ni}^{\text{II}}$  ion, *via* an O atom of the coordinated carboxylate group, resulting in the formation of a two-dimensional layer-like polymer. The remaining coordination sites of the two independent octahedral  $\text{Ni}^{\text{II}}$  ions are occupied by water molecules. The layers are connected *via* hydrogen bonds involving all six coordinated water molecules.

### Comment

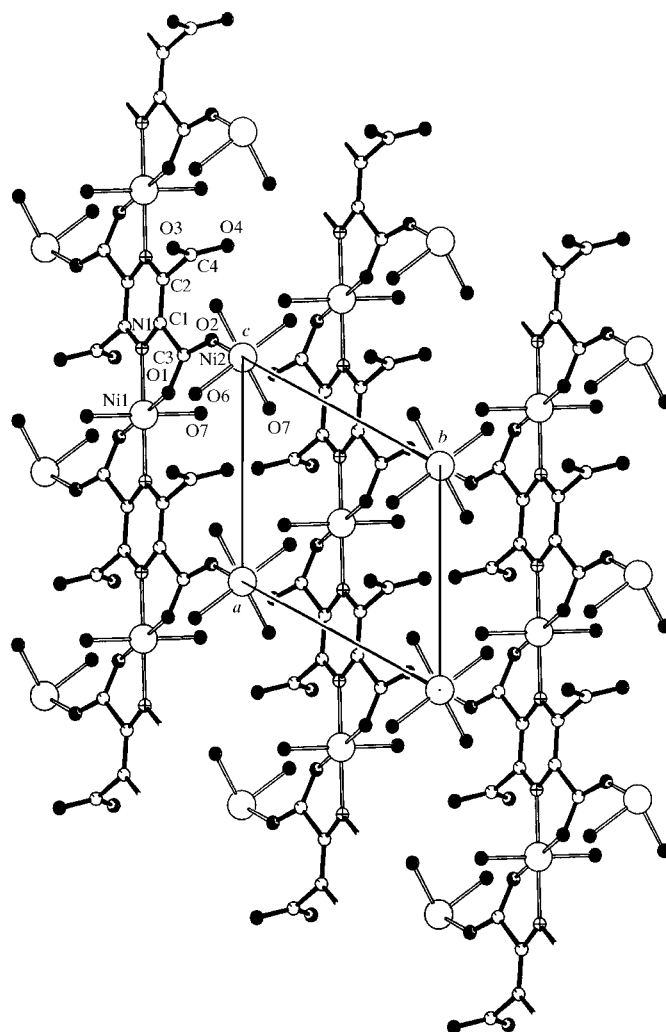
Pyrazine-2,3,5,6-tetracarboxylic acid ( $\text{pztcH}_4$ ) was first synthesized over 100 years ago (Wolff, 1887, 1893) and an alternative synthesis was later proposed by Chattaway & Humphrey (1929). More recently, it has been used to form coordination polymers with first row transition metals, such as iron(II) (Marioni *et al.*, 1986), copper(II) (Graf *et al.*, 1993), manganese(II) (Marioni *et al.*, 1994) and zinc(II) (Marioni *et al.*, 1986). We present here the results of the reaction of  $\text{pztcH}_4$  with  $\text{NiSO}_4$  to form the title coordination polymer, (I), and describe its analysis and structure determination, which were carried out by laboratory X-ray powder diffraction analysis.

Compound (I) is a planar two-dimensional polymer (Fig. 1).  $\text{Ni}^{\text{II}}$  ions are bridged by the deprotonated pyrazine-2,3,5,6-tetracarboxylic acid ( $\text{pztc}^{4-}$ ,  $\text{C}_8\text{N}_2\text{O}_8^{4-}$ ) ligand coordinating in a bis-bidentate manner, so forming one-dimensional polymer chains with coplanar pyrazine rings. The chains are linked by  $[\text{Ni}(\text{H}_2\text{O})_4]^{2+}$  units, with atom Ni2 coordinated to atom O2 of

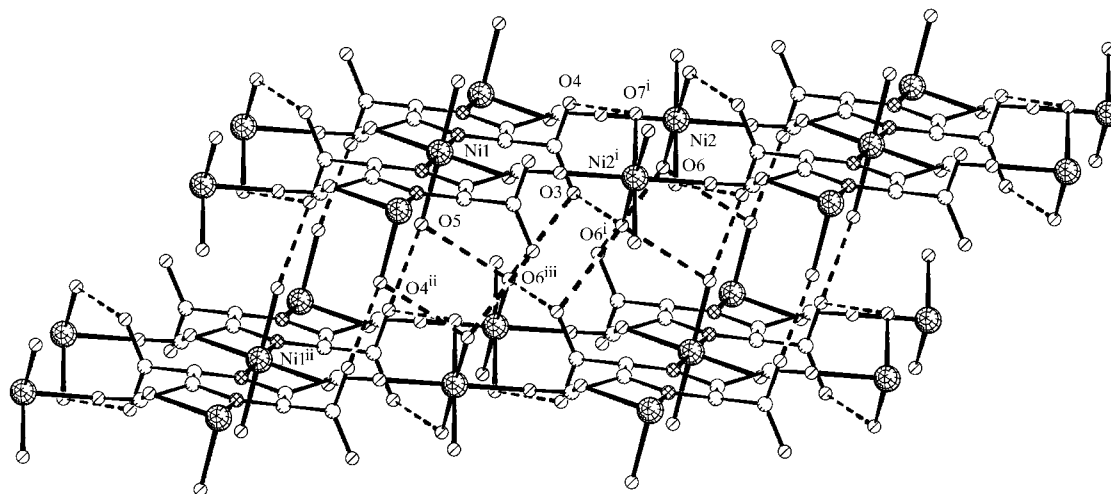
the coordinated carboxylate groups in the chains, resulting in the formation of a two-dimensional sheet-like structure. Selected bond distances and angles, and possible hydrogen-bond  $\text{O}\cdots\text{O}$  distances, are given in Table 1.



The deprotonated centrosymmetric  $\text{pztc}^{4-}$  ligand is coordinated to two crystallographically equivalent  $\text{Ni}^{\text{II}}$  ions (Ni1) through the two N atoms of the pyrazine ring and two O atoms from two symmetrically opposing carboxylate groups. Water molecules occupy the remaining coordination sites of the octahedral Ni1 ions. The metal ions occupy inversion centres and the ligand possesses  $C_i$  symmetry.



**Figure 1**  
PLATON (Spek, 2001) drawing of (I) showing the atom-numbering scheme.

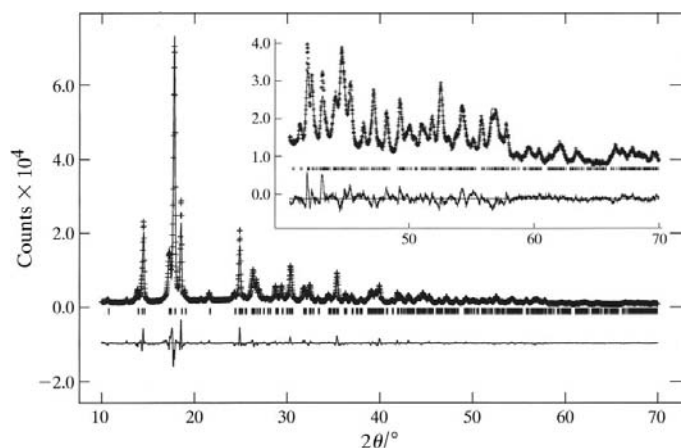


**Figure 2**

A side view of (I) showing the possible intra- and inter-plane hydrogen-bonding network as dashed lines. The symmetry codes are as in Table 1.

The metal-to-metal distance,  $\text{Ni1} \cdots \text{O1} - \text{C3} - \text{O2} \cdots \text{Ni2}$ , is 5.4126 (3) Å, which is shorter than the  $\text{Ni1} - \text{pyrazine} - \text{Ni1}$  ( $1 + x, y, z$ ) distance of 6.989 (1) Å. The  $\text{Ni1} - \text{N1}$  bond [2.082 (1) Å] is slightly longer and the  $\text{Ni2} - \text{O2}$  bond [1.991 (2) Å] slightly shorter than the same distances in similar  $\text{Ni}^{\text{II}}$  complexes with pyrazine-2,3-dicarboxylic acid (mean  $\text{Ni} - \text{N}$  2.061 Å and mean  $\text{Ni} - \text{O}$  2.060 Å; Mao *et al.*, 1996) and pyrazine-2,5-dicarboxylic acid ( $\text{Ni} - \text{N}$  2.033 Å and  $\text{Ni} - \text{O}$  2.068 Å; Ptasiwicz-Bak *et al.*, 1995). Atom Ni2 of the bridging  $[\text{Ni}(\text{H}_2\text{O})_4]^{2+}$  unit forms four short  $\text{Ni} - \text{O}$  bonds [1.991 (2)–1.994 (2) Å] and two long  $\text{Ni} - \text{O}$  bonds [2.002 (5) Å], while for atom Ni1, the  $\text{Ni} - \text{N}$  bonds are longer than the  $\text{Ni} - \text{O}$  distances, *i.e.* 2.082 (2) versus 2.002 (5) Å.

The two non-coordinated carboxylate groups (atoms C2, O3 and O4) and the coordinated water molecules (atoms O5, O6 and O7) are directed into the interlayer space. The short  $\text{O} \cdots \text{O}$  distances (2.56–2.81 Å; Table 1) suggest possible



**Figure 3**

Observed (+) and calculated (–) profiles for the Rietveld refinement for (I). The bottom curve is the difference plot on the same intensity scale. The insert shows the  $2\theta$  range 40–70° magnified by a factor of 20.

hydrogen bonding between the layers, which would lead to the formation of a three-dimensional network (Fig. 2).

Compound (I) was first synthesized in 1986 (Marioni, 1986) and, based on the elemental analysis, which indicated a metal-to-ligand ratio of 2:1, a binuclear complex was proposed. Thermogravimetric analysis indicated the presence of six water molecules. This result supported the proposition of a binuclear  $\text{Ni}^{\text{II}}$  complex containing the  $\text{pztc}^{4-}$  anion coordinating in a bis-bidentate manner, with the remaining coordination sites of the metal atoms being occupied by water molecules. A single-crystal X-ray analysis was not possible, as the compound was always obtained as a microcrystalline powder. Analysis of the laboratory X-ray powder diffraction data has shown that two chemically independent Ni atoms, Ni1 and Ni2, are found interconnected by a completely deprotonated ligand,  $\text{pztc}^{4-}$ , to form a two-dimensional coordination polymer. The deprotonated ligand in the  $\text{Ni} - \text{pztc} - \text{Ni}$  chains has a formal charge of  $-4$ , which is not compensated for by the  $\text{Ni}^{2+}$  ions. As has been observed in other metal complexes of  $\text{pztcH}_4$ , the carboxylate groups adjacent to those coordinated to the first metal are rotated by almost 50° out of the plane of the pyrazine ring. These negatively charged chains are then connected by  $[\text{Ni}(\text{H}_2\text{O})_4]^{2+}$  ions, resulting in the formation of neutral sheets. This charge compensation behaviour, incorporating  $[\text{M}(\text{H}_2\text{O})_n]^{2+}$  units in the structure, has been observed previously in a zinc(II) complex (Hakansson *et al.*, 1993), a series of iron(II) complexes (Laine *et al.*, 1995) and a trinuclear copper(II) complex (Colacio *et al.*, 1993).

## Experimental

A solution of  $\text{NiSO}_4$  (1.03 g, 3.92 mmol) in water (20 ml) was added to an aqueous solution of pyrazine-2,3,5,6-tetracarboxylic acid (0.50 g, 1.95 mmol, 20 ml) at 323 K. The solution was stirred for 5 min at 323 K and then cooled slowly to room temperature. The light-green microcrystalline solid which formed was filtered off after

3 d (yield 0.66 g, 71%). Analysis calculated for  $C_8H_{12}N_2Ni_2O_{14}$ : C 20.12, H 2.53, N 5.87%; found: C 19.42, H 2.54, N 5.73%; IR spectroscopic analysis (KBr,  $\nu$ ,  $cm^{-1}$ ): 3365 (H<sub>2</sub>O), 1645 (C=O), 1443, 1323 (C=N, C=C).

## Crystal data

$[Ni_2(C_8N_2O_8)(H_2O)_6]$	$D_x = 2.188 \text{ Mg m}^{-3}$
$M_r = 477.5$	Cu $K\alpha$ radiation
Triclinic, $P\bar{1}$	$\lambda = 1.5418 \text{ \AA}$
$a = 6.9892(3) \text{ \AA}$	$\mu = 4.10 \text{ mm}^{-1}$
$b = 7.169(4) \text{ \AA}$	$T = 295(2) \text{ K}$
$c = 8.2106(3) \text{ \AA}$	Specimen shape: flat sheet
$\alpha = 85.922(3)^\circ$	$25 \times 25 \times 1 \text{ mm}$
$\beta = 84.242(4)^\circ$	Specimen prepared at 295(2) K
$\gamma = 61.818(3)^\circ$	Particle morphology: plate-like,
$V = 360.65(1) \text{ \AA}^3$	green
$Z = 1$	

## Data collection

Rigaku/AFC diffractometer	$T = 295(2) \text{ K}$
Specimen mounting: packed powder pellet	$2\theta_{\min} = 10, 2\theta_{\max} = 70^\circ$
Specimen mounted in reflection mode	Increment in $2\theta = 0.01^\circ$

## Refinement

$R_p = 0.065$	Profile function: pseudo-Voigt
$R_{wp} = 0.086$	50 parameters
$R_{exp} = 0.019$	H atoms not refined
$S = 1.30$	Weighting scheme: $w = 1/[y(\text{obs})]^{1/2}$
$2\theta_{\min} = 10, 2\theta_{\max} = 70^\circ$	$(\Delta/\sigma)_{\max} = 0.01$
Increment in $2\theta = 0.01^\circ$	Preferred orientation correction:
Wavelength of incident radiation: 1.5418 $\text{\AA}$	none

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Ni1—N1	2.082(1)	Ni2—O7	2.002(2)
Ni1—O1	2.002(2)	O3...O6 <sup>i</sup>	2.80(1)
Ni1—O5	2.002(2)	O4...O5 <sup>ii</sup>	2.56(1)
Ni2—O2	1.991(2)	O4...O7 <sup>i</sup>	2.64(1)
Ni2—O6	1.994(2)	O5...O6 <sup>iii</sup>	2.81(1)
O1—Ni1—N1	76.7(1)	O2—Ni2—O6	91.9(1)
O1—Ni1—N1 <sup>iv</sup>	103.3(1)	O2—Ni2—O6 <sup>v</sup>	88.1(1)
O5—Ni1—N1	87.1(1)	O2—Ni2—O7	93.5(1)
O5—Ni1—N1 <sup>iv</sup>	92.9(1)	O2—Ni2—O7 <sup>v</sup>	86.5(1)
O5—Ni1—O1	89.5(1)	O6—Ni2—O7	90.7(1)
O5—Ni1—O1 <sup>iv</sup>	90.5(1)	O6—Ni2—O7 <sup>v</sup>	89.3(1)

Symmetry codes: (i)  $x-1, y, z$ ; (ii)  $-x, -y, -1-z$ ; (iii)  $x, y, z-1$ ; (iv)  $1-x, -1-y, -1-z$ ; (v)  $-x, -y, -z$ .

The indexing procedure (Visser, 1969) revealed a triclinic cell, which was used for the structure solution. Approximately 400 reflections were extracted from the powder diffraction pattern for use in direct methods. Two independent Ni-atom positions, both occupying special positions, and the coordinating N and O atoms, were located. The structural model was then completed by difference

Fourier techniques. It was not possible to locate the water H atoms. This model was then used for Rietveld profile refinement. After the initial refinement of the scale, background and unit-cell constants, the atomic positions were refined with soft constraints for the pyrazine and carboxylate bond distances (*International Tables for Crystallography*, 1995, Vol. C, pp. 739, 750) and angles, and with a low weight. In the final cycles of refinement, the shifts in all the parameters were less than their s.u.'s. The final Rietveld plot is given in Fig. 3.

Data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku Corporation, 1995); cell refinement: *EXPO* (Altomare *et al.*, 1997); data reduction: *EXPO*; program(s) used to solve structure: *EXPO* and *SHELXL97* (Sheldrick, 1997); program(s) used to refine structure: *GSAS* (Larson & Von Dreele, 1994); molecular graphics: *PLATON* (Spek, 2001); software used to prepare material for publication: *GSAS*.

Financial support from the Swiss National Science Foundation is gratefully acknowledged. We also wish to thank Professor Abraham Clearfield at the Texas A&M University, USA, for enabling the X-ray powder diffraction experiment to be carried out.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1451). Services for accessing these data are described at the back of the journal.

## References

- Altomare, A., Burla, M. C., Cascarano, G., Giacobovazzo, C., Guagliardi, A., Moliterni, A. G. G. & Polidori, G. (1997). *EXPO*. University of Bari, Italy.
- Chattaway, F. D. & Humphrey, W. G. (1929). *J. Chem. Soc.* pp. 645–651.
- Colacio, E., Dominguez-Vera, J.-M., Kivekäs, R., Moreno, J. M., Romerosa, A. & Ruiz, J. (1993). *Inorg. Chim. Acta*, **212**, 115–121.
- Graf, M., Stoeckli-Evans, H., Whitaker, C., Marioni, P.-A. & Marty, W. (1993). *Chimia*, **47**, 198–202.
- Hakansson, K., Lindahl, M., Svensson, G. & Albertsson, J. (1993). *Acta Chem. Scand.* **47**, 449–455.
- Laine, P., Gourdon, A. & Launay, J.-P. (1995). *Inorg. Chem.* **34**, 5138–5149.
- Larson, A. & Von Dreele, R. B. (1994). *GSAS*. Los Alamos National Laboratory, New Mexico, USA.
- Mao, L., Rettig, S. J., Thompson, R. C., Trotter, J. & Xia, S. (1996). *Can. J. Chem.* **74**, 433–444.
- Marioni, P. A. (1986). PhD Thesis, Université de Neuchâtel, Switzerland.
- Marioni, P.-A., Marty, W., Stoeckli-Evans, H. & Whitaker, C. (1994). *Inorg. Chim. Acta*, **219**, 161–168.
- Marioni, P.-A., Stoeckli-Evans, H., Marty, W., Güdel, H.-U. & Williams, A. F. (1986). *Helv. Chim. Acta*, **69**, 1004–1011.
- Ptasiewicz-Bak, H., Leciejewicz, J. & Zachara, J. (1995). *J. Coord. Chem.* **36**, 317–326.
- Rigaku Corporation (1995). *Rigaku/AFC Diffractometer Control Software*. Version 5.32b. Rigaku Corporation, Tokyo, Japan.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2001). *PLATON*. University of Utrecht, The Netherlands.
- Visser, J. W. (1969). *J. Appl. Cryst.* **2**, 89–95.
- Wolff, L. (1887). *Ber. Dtsch. Chem. Ges.* **20**, 425–429.
- Wolff, L. (1893). *Ber. Dtsch. Chem. Ges.* **26**, 721–725.