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# *catena*-Poly[[[aqua(di-2-pyridylamine-$\kappa^2N,N'$)-nickel(II)]-$\mu$-4-aminobenzoato-$\kappa^3O,O':N$] chloride trihydrate]

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**Key indicators**

Single-crystal X-ray study
*T* = 123 K
Mean $\sigma$(C–C) = 0.005 Å
*R* factor = 0.035
*wR* factor = 0.086
Data-to-parameter ratio = 17.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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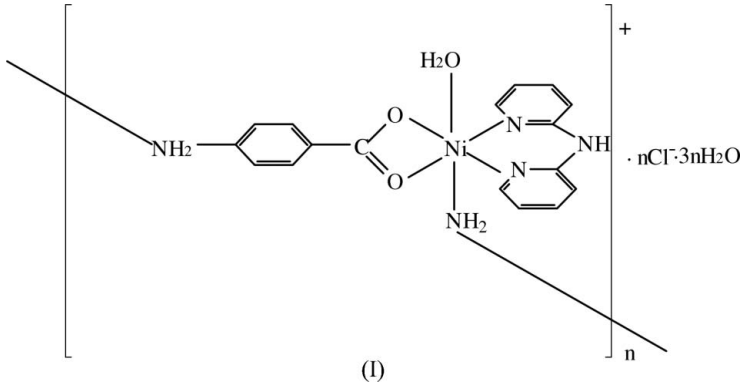
The title complex, $[Ni(C_7H_6NO_2)(C_{10}H_9N_3)(H_2O)]Cl\cdot 3H_2O$, has a zigzag polymeric structure. Each Ni ion is bonded to two N atoms from a di-2-pyridylamine (BPA) ligand, two O atoms from a 4-aminobenzoic acid (*p*-AB) ligand, one water O atom and one amino N atom from another *p*-AB ligand. This is the first example of an aromatic amino N acting in a bridging role linking adjacent molecules to form a chain structure. Three water molecules and one chloride ion are also in the asymmetric unit. There are several hydrogen bonds stabilizing the crystal structure.

## Comment

4-Aminobenzoic acid (*p*-AB) is an essential nutrient for some bacteria and is sometimes called Vitamin H′. It is well known to be a potent natural antimutagen (Vasilieva, 2001). *p*-AB is an interesting ligand because it shows various coordination modes. In order to understand the interaction between biological ligands and metal ions, several complexes including *p*-AB have been synthesized and their crystal structures have been studied, including $Cu^{II}$, $Ag^{I}$, $Zn^{II}$ complexes (Wang & Okabe, 2005*a*; Wang, Jiang *et al.*, 2005; Wang *et al.*, 2004). In this study, a novel amino-bridged $Ni^{II}$ polymeric complex, (I), is reported.




(I)

Compound (I) contains an $[Ni(p\text{-AB})(BPA)(H_2O)]^+$ cation, a chloride anion and three water molecules in the asymmetric unit (Fig. 1). Each $Ni^{II}$ is coordinated by two carboxylate O atoms from the *p*-AB ligand, two N atoms from the BPA ligand, one water O atom, and one amino N atom from an adjacent *p*-AB (symmetry code: $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$). Geometric details are given in Table 1. The Ni—O(water) bond length is within the normal range for such bonds (Wang & Okabe, 2005*b*; Cheng *et al.*, 2003; Wang, Song & Zhang, 2005), while the bond Ni—N4$^{i}$ [symmetry code: (i) $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$] is slightly elongated, thus generating a slightly

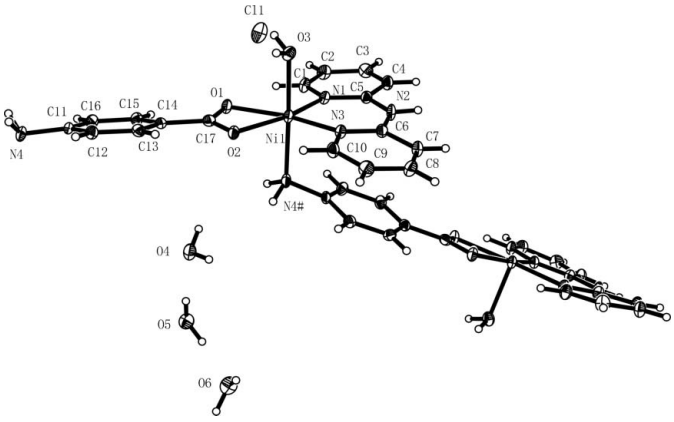



**Figure 1**
*ORTEP-3* (Farrugia, 1997) drawing of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Atom N4# and unlabelled atoms are related to labelled atoms by the symmetry operation $(-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$.

distorted octahedral geometry, with two N and two O atoms occupying the equatorial plane, and the water O atom and atom N4 occupying the axial positions.

The structure of (I) is similar to that of the complex [Ni(*p*-HB)(BPA)$(H_2O)_2$]Cl (Wang & Okabe, 2005*b*), in which the $Ni^{II}$ ion has a distorted octahedral coordination, being connected to two carboxylate O atom from a *p*-HB (4-hydroxybenzoic acid) ligand [Ni—O = 2.099 (1) and 2.142 (2) Å], two N atoms from BPA [Ni—N = 2.010 (2) and 2.012 (2) Å] and two water O atoms [Ni—O = 2.089 (1) and 2.117 (1) Å]. In the case of (I), adjacent units form an infinite zigzag chain along the *a*-axis direction, which is very rare among *p*-AB complexes. Here, *p*-AB acts as a tridentate ligand, very different from its typical bidentate role when the amino N atom is not involved in the coordination (Wang & Okabe, 2005*a*; Wang *et al.*, 2004). The structure of the polymer is shown in Fig. 2. In addition to the water molecule bonded to Ni, there are three further water molecules and one $Cl^-$ ion in the asymmetric unit. The chains are held together by a network of hydrogen bonds involving the coordinated water molecule, the uncoordinated water, the chloride ion and the carboxylate O atom of the ligand (Table 2).

## Experimental

Pale-green platelet crystals of (I) were obtained by slow evaporation of an aqueous 80% (*v*/*v*) methanol solution of a mixture of *p*-aminobenzolic acid, 2,2′-bipyridineamine and $NiCl_2$ (molar ratio 1:1:1) at room temperature.

*Crystal data*

| | |
|---|---|
| $[Ni(C_7H_6NO_2)(C_{10}H_9N_3)(H_2O)]Cl\cdot 3H_2O$ | $V$ = 2000 (4) Å$^3$ |
| $M_r$ = 473.53 | $Z$ = 4 |
| Monoclinic, $P2_1/n$ | $D_x$ = 1.573 Mg m$^{-3}$ |
| $a$ = 11.28 (1) Å | Mo $K\alpha$ radiation |
| $b$ = 14.51 (1) Å | $\mu$ = 1.15 mm$^{-1}$ |
| $c$ = 12.22 (2) Å | $T$ = 123.1 K |
| $\beta$ = 90.11 (5)° | Platelet, pale-green |
| | 0.10 × 0.10 × 0.05 mm |

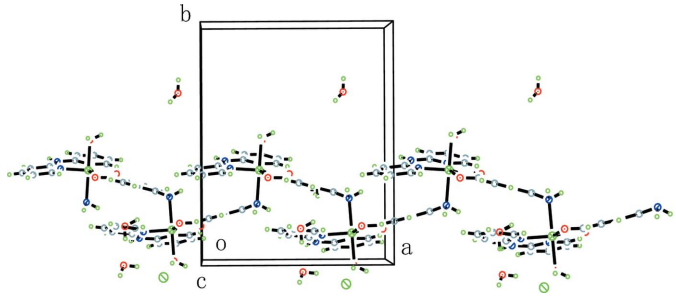



**Figure 2**
Partial packing diagram of (I).

*Data collection*

| | |
|---|---|
| Rigaku R-AXIS RAPID diffractometer | 19036 measured reflections |
| $\omega$ scans | 4570 independent reflections |
| Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995) | 2151 reflections with $F^2 > 2\sigma(F^2)$ |
| $T_{min}$ = 0.899, $T_{max}$ = 0.944 | $R_{int}$ = 0.062 |
| | $\theta_{max}$ = 27.5° |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)]$ = 0.035 | $w = 1/[\sigma^2(F_o^2) + (0.0449P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2)$ = 0.086 | $(\Delta/\sigma)_{max} < 0.001$ |
| $S$ = 0.84 | $\Delta\rho_{max}$ = 0.37 e Å$^{-3}$ |
| 4570 reflections | $\Delta\rho_{min}$ = −0.59 e Å$^{-3}$ |
| 262 parameters | |

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Ni1—N3 | 2.007 (3) | Ni1—O1 | 2.109 (3) |
| Ni1—N1 | 2.016 (3) | Ni1—O2 | 2.139 (3) |
| Ni1—O3 | 2.099 (3) | Ni1—N4$^{i}$ | 2.204 (3) |
| | | | |
| N3—Ni1—N1 | 92.95 (11) | O3—Ni1—O2 | 90.29 (8) |
| N3—Ni1—O3 | 90.07 (9) | O1—Ni1—O2 | 62.27 (8) |
| N1—Ni1—O3 | 90.26 (9) | N3—Ni1—N4$^{i}$ | 89.66 (9) |
| N3—Ni1—O1 | 165.08 (8) | N1—Ni1—N4$^{i}$ | 92.71 (10) |
| N1—Ni1—O1 | 101.97 (10) | O3—Ni1—N4$^{i}$ | 177.02 (8) |
| O3—Ni1—O1 | 90.35 (8) | O1—Ni1—N4$^{i}$ | 89.14 (8) |
| N3—Ni1—O2 | 102.81 (10) | O2—Ni1—N4$^{i}$ | 86.88 (9) |
| N1—Ni1—O2 | 164.24 (9) | | |

Symmetry code: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$.

**Table 2**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H5···O4$^{i}$ | 0.86 | 2.01 | 2.863 (4) | 172 |
| N4—H15···Cl1$^{ii}$ | 0.97 | 2.538 | 3.492 (4) | 169 |
| O3—H16···O1$^{iii}$ | 0.90 | 1.93 | 2.805 (4) | 165 |
| O3—H17···Cl1 | 0.90 | 2.26 | 3.124 (4) | 161 |
| O4—H18···O5$^{iv}$ | 0.90 | 1.93 | 2.799 (4) | 162 |
| O4—H19···Cl1$^{v}$ | 0.90 | 2.20 | 3.075 (4) | 165 |
| O5—H20···O4 | 0.91 | 1.91 | 2.806 (4) | 170 |
| O5—H21···O6 | 0.91 | 1.91 | 2.811 (4) | 170 |
| O6—H22···O2$^{v}$ | 0.91 | 2.13 | 2.977 (4) | 155 |
| O6—H23···Cl1$^{vi}$ | 0.92 | 2.29 | 3.195 (3) | 167 |

Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $-x+1, -y, -z$; (iii) $-x, -y, -z$; (iv) $-x, -y+1, -z$; (v) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (vi) $x, y+1, z$.

All H atoms were located in difference Fourier maps, then positioned geometrically and treated as riding, with C—H distances of 0.93 Å, N—H distances ranging from 0.86 to 0.97 Å and O—H distances of 0.91 Å and with $U_{iso}(H) = 1.2U_{eq}$ of the carrier atom.

Data collection: *PROCESS-AUTO* (Rigaku, 2003); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999)'; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

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## References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Cheng, D. P., Khan, M. A. & Houser, R. P. (2003). *Inorg. Chim. Acta*, **351**, 242–250.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.

Rigaku (2003). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.

Rigaku/MSC (2004). *Crystal Structure*. Version 3.60. Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Vasilieva S. (2001). *Mutat. Res.* **496**, 89–95.

Wang, R. H., Hong, M. C., Luo, J. H., Jiang, F. L., Han, L., Lin, Z. Z. & Cao, R. (2004). *Inorg. Chim. Acta*, **357**, 103–114.

Wang, R. H., Jiang, F. L., Zhou, Y. F., Han, L. & Hong, M. C. (2005). *Inorg. Chim. Acta*, **358**, 545–554.

Wang, Y. H., Song, R. F. & Zhang, F. Y. (2005). *J. Mol. Struct.* **752**, 104–109.

Wang, Y. & Okabe, N. (2005*a*). *Chem. Pharm. Bull.* **53**, 645–652.

Wang, Y. & Okabe, N. (2005*b*). *Inorg. Chim. Acta*, **358**, 3407–3416.