

van der Waals radii of 3.79 Å (Bondi, 1964) and indicate the bidentate chelating nature of the carboxylate groups of the ligand. The relatively small value of the angle O(1)—Sn(1)—O(2) of 83.5 (2)° and the large value of O(3)—Sn(1)—O(4) of 167.1 (2)° could be caused by lattice effects. Each ligand links two Sn centers *via* the carboxylate groups to form a zigzag chain. This type of chain formation is unusual and is possibly caused by the substitution pattern of two carboxylate groups on one C atom of the ligand.

The cyclobutane ring is nearly planar. The displacement parameters  $U_{ik}$  of C(3) point to strong 'vibration' ( $r_{\max}/r_{\min} = 8.1$ ) perpendicular to the plane of the ring; the fact that the atoms C(2) and C(4) which are bound to C(3) show normal temperature factors ( $r_{\max}/r_{\min} = 2.2$  and 2.4) indicates orientational disorder (dynamic puckering) for the position C(3) as has been found in *cis*-diammine(1,1-cyclobutanedicarboxylato)platinum(II) (Beagley, Cruickshank, McAuliffe, Pritchard, Zaki, Beddoes, Cernik & Mills, 1985). Distances between the chains smaller than the sum of the van der Waals radii do not exist.

Financial assistance by Fonds der Chemischen Industrie is gratefully acknowledged.

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*Acta Cryst.* (1990). **C46**, 2073–2075

## Structure of Bis(glycinato- $\kappa N, \kappa O$ )(2,2'-bipyridyl- $\kappa^2 N, N'$ )nickel(II) 5.5-Hydrate

BY Z. ŽÁK

*Department of Inorganic Chemistry, Masaryk University, Kotlářská 2, 611 37 Brno, Czechoslovakia*

T. GŁOWIAK

*Institute of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland*

J. KAMENÍČEK

*Department of Inorganic and Physical Chemistry, Palacký University, Křížkovského 10, 771 47 Olomouc, Czechoslovakia*

AND F. BŘEZINA

*Department of Inorganic and Physical Chemistry, Palacký University, Křížkovského 10, 771 47 Olomouc, Czechoslovakia*

(Received 27 November 1989; accepted 14 March 1990)

**Abstract.**  $[\text{Ni}(\text{C}_2\text{H}_4\text{NO}_2)_2(\text{C}_{10}\text{H}_8\text{N}_2)] \cdot 5.5\text{H}_2\text{O}$ , orthorhombic, *Fdd2*,  $a = 28.181$  (4),  $b = 40.267$  (7),  $c = 7.461$  (2) Å,  $V = 8466$  (3) Å<sup>3</sup>,  $F(000) = 3888$ ,  $M_r = 462.1$ ,  $Z = 16$ ,  $D_m = 1.430$ ,  $D_x = 1.450$  Mg m<sup>-3</sup>, graphite-monochromated Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å,  $T = 298$  K. The structure was solved by the heavy-atom method and refined to  $R = 0.040$ ,  $wR$

$= 0.049$ , for 2469 significant independent reflexions. The coordination about the Ni atom is a distorted octahedron in which the two Ni—N(gly) distances differ significantly, 2.065 (4) and 2.145 (5) Å. The crystal structure contains an extended network of hydrogen bonds involving water—O(gly), water—N(gly), and water—water interactions.

**Introduction.** The compounds of a general formula (gly<sub>2</sub>N-N)Ni·*n*H<sub>2</sub>O, (where gly = glycine anion and N-N = ethylenediamine, 1,10-phenanthroline, and 2,2'-bipyridine), can be prepared by the substitution of water molecules in [gly<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]Ni (Březina, Šindelář, Kameníček & Lasovský, 1988) by an appropriate bidentate ligand. Because the water molecules in [gly<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]Ni are in the *trans* position (Stosick, 1945; Freeman & Guss, 1968) their substitution by a bidentate ligand may lead to the formation of polynuclear complex species. However, the temperature dependence of the magnetic susceptibility of such compounds suggests a reorganization of the coordination polyhedron about Ni and the formation of mononuclear complexes of Ni<sup>II</sup>. The title compound was chosen as representative of these compounds for the crystal and molecular structure determination, the results of which are presented in this communication.

**Experimental.** The crystals suitable for X-ray work were obtained by recrystallization of the compound from water. Experimental density was obtained by flotation in a CH<sub>2</sub>I<sub>2</sub>-benzene mixture. Preliminary lattice parameters and the space group were determined from Weissenberg and precession photographs. Final lattice parameters were refined from 15 reflexions, 16 < 2θ < 26°, collected on Syntex P2<sub>1</sub> diffractometer.

The intensities of 3427 independent reflexions were collected by the θ-2θ scan technique up to 2θ = 60°, 0 < *h* < 38, 0 < *k* < 56, 0 < *l* < 9. The crystal used for the intensity measurements was of dimensions 0.6 × 0.6 × 0.7 mm. The intensities were corrected for Lorentz-polarization and absorption effects. The minimum and maximum values of the absorption were 0.834 and 1.356, respectively. The stability of the crystal during the data collection was checked by measuring two standard reflexions after every 50 measured but no significant decrease in their intensities was detected. From the total of the reflexions measured, only 2469 with *I* > 3.5σ(*I*) were used for the structure solution and refinement.

The structure was solved by the heavy-atom method and the refinement was performed by a block-diagonal matrix least-squares method with weights *w* = 1/σ<sup>2</sup>(*F*<sub>o</sub>) on |*F*<sub>o</sub>|. Non-H atoms were refined anisotropically. The H atoms were placed at calculated positions 1.0 Å from the atoms to which they are bonded and were arbitrarily assigned isotropic temperature factors *B* = 6.0 Å<sup>2</sup> for the H atoms of the water molecules and *B* = 5.0 Å<sup>2</sup> for the rest, and were not refined. The refinement was stopped when Δ/σ < 0.3. The final *R* and *wR* values are 0.040 and 0.049, respectively (including unobserved reflexions 0.041 and 0.058, respectively), *S* = 3.06. A final electron density map showed maximum

Table 1. The final atomic parameters (× 10<sup>4</sup>) and *B*<sub>eq</sub> values and their *e.s.d.*'s in parentheses

$$B_{eq} = 1/3(B_{11} + B_{22} + B_{33}).$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> (Å <sup>2</sup> )
Ni	1404.0 (2)	885.0 (1)	2200.0	1.80 (2)
O(1)	1123 (1)	1321 (1)	3251 (5)	2.7 (2)
O(2)	1190 (1)	1711 (1)	5323 (6)	3.5 (2)
O(3)	0895 (1)	0616 (1)	3610 (5)	2.5 (2)
O(4)	0153 (1)	0439 (1)	3482 (6)	3.4 (2)
W1	0	0	6141 (8)	3.5 (3)
W2	0963 (2)	1927 (2)	8854 (7)	6.6 (3)
W3	0372 (1)	1586 (1)	1234 (7)	4.4 (2)
W4	0836 (2)	-0157 (1)	8005 (7)	4.4 (2)
W5	1200 (2)	0486 (1)	7043 (6)	4.1 (2)
W6	1828 (1)	2200 (1)	4061 (7)	4.7 (2)
N(1)	1818 (1)	0928 (1)	4602 (7)	2.6 (2)
N(2)	0886 (1)	0874 (1)	0244 (6)	2.4 (2)
N(11)	1758 (1)	0473 (1)	1239 (6)	2.1 (2)
N(12)	1913 (1)	1112 (1)	0685 (6)	2.2 (2)
C(1)	1314 (2)	1441 (1)	4621 (8)	2.5 (2)
C(2)	1723 (2)	1249 (2)	5474 (9)	3.7 (3)
C(3)	0507 (2)	0567 (1)	2794 (7)	2.3 (2)
C(4)	0479 (2)	0662 (2)	0837 (8)	3.9 (3)
C(11)	1630 (2)	0157 (1)	1456 (9)	2.9 (2)
C(12)	1864 (2)	-0101 (1)	0618 (9)	3.4 (3)
C(13)	2238 (2)	-0029 (2)	-0486 (10)	4.6 (3)
C(14)	2381 (2)	0300 (2)	-0707 (10)	4.0 (3)
C(15)	2128 (2)	0546 (1)	0140 (7)	2.3 (2)
C(16)	2229 (2)	0903 (1)	-0107 (7)	2.2 (2)
C(17)	2607 (2)	1022 (1)	-1086 (8)	2.8 (2)
C(18)	2669 (2)	1363 (1)	-1266 (8)	3.2 (3)
C(19)	2348 (2)	1575 (1)	-0504 (9)	3.3 (3)
C(110)	1975 (2)	1444 (1)	0479 (8)	2.7 (2)

Table 2. Selected interatomic distances (Å) and bond angles (°)

Ni—O(1)	2.079 (4)	N(11)—C(15)	1.359 (7)
Ni—O(3)	2.083 (4)	N(12)—C(16)	1.360 (6)
Ni—N(1)	2.145 (5)	N(11)—C(11)	1.332 (6)
Ni—N(2)	2.065 (4)	N(12)—C(110)	1.357 (6)
Ni—N(11)	2.064 (4)	C(11)—C(12)	1.380 (7)
Ni—N(12)	2.042 (4)	C(110)—C(19)	1.386 (8)
O(1)—C(1)	1.252 (7)	C(12)—C(13)	1.369 (9)
O(3)—C(3)	1.267 (6)	C(19)—C(18)	1.368 (7)
C(1)—O(2)	1.256 (6)	C(13)—C(14)	1.395 (10)
C(3)—O(4)	1.235 (6)	C(18)—C(17)	1.391 (6)
C(1)—C(2)	1.527 (9)	C(14)—C(15)	1.374 (9)
C(3)—C(4)	1.511 (8)	C(17)—C(16)	1.378 (8)
C(2)—N(1)	1.472 (9)	C(15)—C(16)	1.475 (7)
C(4)—N(2)	1.497 (7)		
O(1)—Ni—O(3)	89.2 (1)	N(11)—Ni—N(12)	80.1 (2)
O(1)—Ni—N(1)	79.9 (1)	O(1)—C(1)—O(2)	123.7 (5)
O(1)—Ni—N(2)	90.9 (1)	O(3)—C(3)—O(4)	124.2 (5)
O(1)—Ni—N(11)	173.5 (3)	O(1)—C(1)—C(2)	118.0 (5)
O(1)—Ni—N(12)	95.6 (2)	O(3)—C(3)—C(4)	118.0 (5)
O(3)—Ni—N(1)	89.7 (1)	O(2)—C(1)—C(2)	118.3 (5)
O(3)—Ni—N(2)	81.9 (1)	O(4)—C(3)—C(4)	117.7 (5)
O(3)—Ni—N(11)	95.2 (2)	C(1)—C(2)—N(1)	113.4 (5)
O(3)—Ni—N(12)	174.9 (6)	C(3)—C(4)—N(2)	112.9 (4)
N(1)—Ni—N(2)	167.6 (4)	C(11)—N(11)—C(15)	119.2 (4)
N(1)—Ni—N(11)	95.3 (2)	C(110)—N(12)—C(16)	118.4 (4)
N(1)—Ni—N(12)	92.5 (2)	N(11)—C(15)—C(16)	115.7 (4)
N(2)—Ni—N(11)	94.5 (2)	N(12)—C(16)—C(15)	114.9 (4)
N(2)—Ni—N(12)	96.6 (2)		

and minimum residual density of 0.32 and -0.24 e Å<sup>-3</sup>. The programs employed during the structure solution and refinement, including atomic scattering factors, were a part of the XTL program

system supplied by the Syntex Corporation (Syntex, 1973). For the Ni atom, anomalous dispersion was taken into account. The configuration of the molecule was determined from two simultaneous runs of least-squares refinement with the structure and its enantiomorph. The model which yielded a significantly lower value of  $R$  was accepted as the correct configuration.

**Discussion.** The final atomic parameters with equivalent isotropic thermal parameters are listed in Table 1; selected bond lengths and angles are given in Table 2.\*

The structure is composed of discrete molecules of the Ni complex, linked by a network of hydrogen-bonded water molecules. In the molecule the arrangement of the ligands about the Ni atom is distorted octahedral as shown in Fig. 1. The two Ni—N(gly) distances, Ni—N(1) = 2.145 (5) and Ni—N(2) = 2.065 (4) Å, differ substantially and represent the extremes of the range of Ni—N(amino) bond lengths found in related structures. Thus, values of 2.067 (2) and 2.149 Å have been reported for [gly<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>Ni] (Castellano, Nascimento & Calvo, 1982) and Na<sub>2</sub>[(gly.gly)<sub>2</sub>Ni].*n*H<sub>2</sub>O where  $n = 8$  and 9 (Freeman & Guss, 1978) respectively. The Ni—O(gly) distances, however, are identical within experimental error and compare with values of 2.077 (2) Å in [gly<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>Ni] (Castellano *et al.*, 1982) and 2.161–2.186 (3) Å in Na<sub>2</sub>[(gly.gly)<sub>2</sub>Ni].*n*H<sub>2</sub>O (Freeman & Guss, 1978). The Ni—N(bpy) distances, 2.064 (4) and 2.042 (4) Å, differ by five e.s.d.'s and are at the lower end of the range found in other complexes of Ni<sup>II</sup> with bipyridine: 2.08–2.10 (1) Å in [Ni(bpy)<sub>3</sub>]SO<sub>4</sub>·7.5H<sub>2</sub>O

(Wada, Sakabe & Tanaka, 1976), 2.063 (3) Å in {[MeO)<sub>2</sub>PS<sub>2</sub>]<sub>2</sub>bpy}Ni (Arora, Carter, Fernando & Seff, 1977) and 2.062 (6) Å in [bpy(H<sub>2</sub>O)<sub>2</sub>SO<sub>4</sub>]Ni (Tedenac & Philippot, 1974).

In the solid state, the 2,2'-bipyridine molecule is planar with the two N atoms in a *trans* configuration (Merritt & Schroeder, 1956; Chisholm, Huffman, Rothwell, Bradley, Kress & Woodruff, 1981). In the present compound, the 2,2'-bipyridine acts as a bidentate ligand, causing the N atoms to adopt a *cis* configuration by rotation about the bond connecting the two pyridine rings. Both pyridine rings are planar within experimental error, but are inclined at a dihedral angle of 7.1 (2)° with respect to one another. Twist angles ranging from 4.3° in [(bpy)ZnCl<sub>2</sub>] (Khan & Tuck, 1984) to 10.9° in [Ni(bpy)<sub>3</sub>]SO<sub>4</sub>·7.5H<sub>2</sub>O (Wada *et al.*, 1976) have been reported. The bond lengths and angles within the bipyridine moiety including the connecting bond, C(15)—C(16) = 1.475 (7) Å, are typical of those observed in other bipyridine complexes.

The geometry of the glycine ligands is closely similar to that found in glycine itself (Marsh, 1958), (gly<sub>2</sub>Cu).H<sub>2</sub>O (Freeman, Snow, Nitta & Tomita, 1964) and [gly<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>Ni] (Castellano *et al.*, 1982).

In the crystal structure there is an extensive hydrogen-bonding network involving water—O(gly), water—N(gly) and water—water interactions: C(water)—O(gly), O(water)—N(gly) and O(water)—O(water) separations are in the ranges 2.692–2.847 (6), 2.988–3.296 (6) and 2.754–2.868 (8) Å, respectively.

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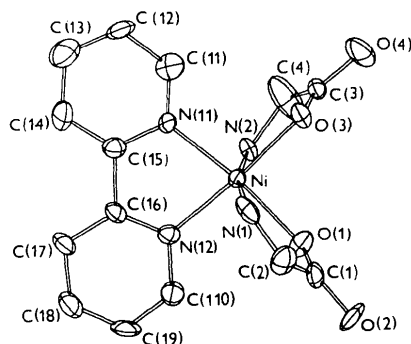


Fig. 1. A perspective view of the molecule of (gly<sub>2</sub>bpy)Ni·5.5H<sub>2</sub>O. H atoms are omitted for clarity; water molecules are not shown.