Inorganica Chimica Acta, *90* (1984) 17–24

Studies on the Metal–Amide Bond. XVIII*. The Crystal and Molecular Structure of [N,N'-bis(2'-pyridinecarboxamido)-1,3-propane] nickel(II) Monohydrate

FREDERICK S. STEPHENS and ROBERT S. VAGG

School of Chemistry, Macquarie University, North Ryde, N.S.W. 2113, Australia

Received February 20, 1984

[N,N'-bis(2'-pyridinecarboxamido)-1,3-propane]-nickel(II) monohydrate, $C_{15}H_{16}N_4O_3Ni$ is monoclinic, space group $P2_1/c$, with a = 7.174(4), b = 18.590(3), c = 11.641(5) Å, β = 110.69(2)°, Z = 4. The structure was refined to R = 0.030 for 1826 diffractometer data using full-matrix least-squares methods. The N_4-ligand coordinates to the nickel atom in an irregular square plane [average $Ni–N_{amide}$ 1.864(4), $Ni–N_{pyridine}$ 1.912(3) Å and $N_{amide}–Ni–N_{amide}$ 96.0(1), $N_{pyridine}–Ni–N_{pyridine}$ 98.7(1)°] with a tetrahedral twist of 15.9° at the nickel atom. The two picolinamide units are related by an approximate two-fold axis and the enforced strain in the molecule results in significant non-planar distortions in the amide chelate rings and the pyridyl rings. The plane of the chelate molecule lies approximately perpendicular to [100] and the lattice water molecule hydrogen bonds amide oxygen atoms to form chains parallel to [101].

Introduction

The ligand, N,N'-bis(2'-pyridinecarboxamide)-1,3-propane, bppnH_2, coordinates to a metal ion on deprotonation to generate a 5-,6-,5-membered chelate ring system. Structural studies of the bivalent copper complexes [1, 2] have shown that as expected the 'B-strain' [3] effect of N_4-planar coordination of the ligand is more pronounced than that for related ligands generating a 5-,5-,5-membered chelate ring system.

The structure of the nickel complex of N,N'-bis-(2'-pyridinecarboxamide)-1,2-ethane, bpenH_2, has been shown [4] to have a closely square planar arrangement about the nickel atom with little distortion in the ligand. In the structure of the analogous complex with N,N'-bis(2'-pyridinecarboxamide)-*trans*-1,2-cyclohexane, *trans*-bpchH_2, [5] distortions within the ligand and a small tetrahedral twist at the nickel atom are evident. A similar diamagnetic complex is formed with bppnH_2 in which distortions from planarity should be much more pronounced. We here report the crystal structure analysis of Ni(bppn)H_2O.

Experimental

Crystal Data

$C_{15}H_{16}N_4O_3Ni$, $M_{\pm}$ = 359.0, Monoclinic, *a* = 7.174(4), *b* = 18.590(3), *c* = 11.641(5) Å, β = 110.69(2)°, *U* = 1452 Å^3, *Z* = 4, *Dc* = 1.642 Mg m^{-3}, *F*(000) = 744, μ(Mo-K_α) = 1.36 mm^{-1}. Systematic absences: 0*k*0 if $k \neq 2n$ and *h*0*l* if $l \neq 2n$, space group $P2_1/c$ (No. 14).

The complex crystallises as orange plates lying on (100) with [001] elongation. Initially unit cell parameters were determined from single crystal oscillation and Weissenberg photographs using Cu-K_α radiation. Accurate cell parameters were obtained from a least-squares fit to diffractometer data. Intensities were collected on an Enraf-Nonius CAD4 diffractometer using graphite monochromatised Mo-K_α radiation. Of the 2548 reflexions recorded 1826 gave counts for which $I > 3\sigma(I)$ and these were used for the structure determination. The intensities were corrected for Lorentz, polarisation and absorption effects.

Neutral-atom scattering factors were taken from 'International Tables for X-ray Crystallography' [6]. All calculations were carried out on a UNIVAC 1106 computer with programmes written by F.S.S.

The structure was solved by the heavy-atom method and refined by a full-matrix least-squares procedure in which the function minimised was $\Sigma w\Delta^2$. The weight, *w*, for each reflexion was initially given by $w = 1/|F_0|$ and in the final stages was that obtained from counting statistics. The refinement included positional parameters for all atoms and anisotropic thermal parameters for the non-hydrogen atoms. Refinement was terminated when the maximum shift in any parameter was $<0.1\sigma$. The final value for *R* was 0.030 and for *R'* [$=(\Sigma w\Delta^2/\Sigma w|F_0|^2)^{1/2}$] was 0.038. A final difference map

---

*Part XVII, is reference [2].

0020-1693/84/$3.00

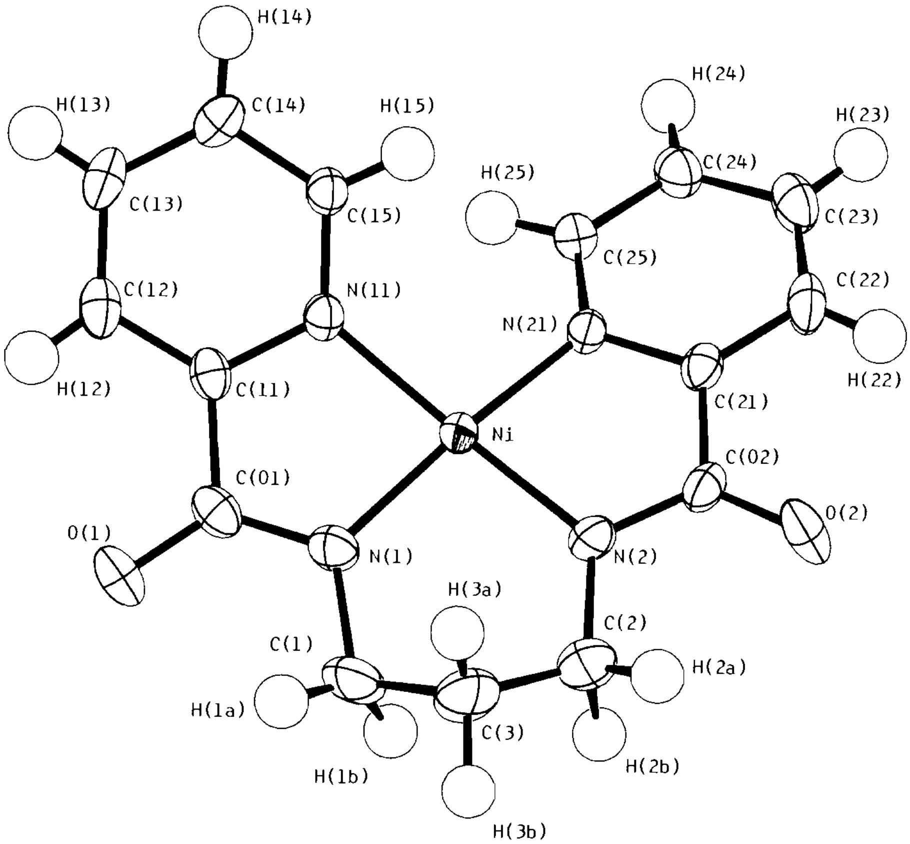

Fig. 1. A perspective drawing of the [Ni(bppn)] molecule together with the atom labelling. Thermal ellipsoids are drawn to include 35% probability.

TABLE I. Final Non-Hydrogen Atomic Coordinates (fractional $\times 10^4$) with Estimated Standard Deviations in Parentheses.

	x	*y*	*z*
Ni	226.8(5)	2000.0(2)	2540.7(3)
N(11)	−1334(3)	2647(1)	1295(2)
N(21)	1712(3)	2693(1)	3728(2)
N(1)	−716(4)	1309(1)	1315(3)
N(2)	1274(4)	1350(1)	3832(2)
C(11)	−1966(4)	2342(2)	167(3)
C(12)	−3067(5)	2719(2)	−866(3)
C(13)	−3621(5)	3420(2)	−745(3)
C(14)	−3085(4)	3715(2)	409(3)
C(15)	−1937(4)	3319(2)	1411(3)
C(O1)	−1517(4)	1557(2)	175(3)
O(1)	−1963(4)	1215(1)	−809(2)
C(1)	−331(8)	532(2)	1479(4)
C(2)	1163(7)	564(2)	3787(4)
C(3)	−395(7)	288(2)	2693(4)
C(O2)	2059(5)	1637(2)	4940(3)
O(2)	2608(4)	1324(1)	5954(2)
C(21)	2385(4)	2431(2)	4880(3)
C(22)	3423(5)	2843(2)	5875(3)
C(23)	3893(5)	3545(2)	5693(3)
C(24)	3346(5)	3800(2)	4513(3)
C(25)	2243(4)	3364(2)	3545(3)
O(W)	5206(4)	259(2)	7497(3)

showed no unusual features with all electron density $<|0.4|\,e\text{Å}^{-3}$.

The final atomic parameters are given in Tables I–III. A list of structure factors has been deposited with the Editor.

Discussion

Figure 1 shows a perspective drawing [7] of the chelate molecule with the atom labelling scheme. The bond lengths and angles are given in Table IV. The planes of the chelate molecules lie approximately perpendicular to [100] and the water molecules hydrogen bond to amide oxygen atoms to form chains parallel to (101). The packing of the molecules in the unit cell is shown in Fig. 2 together with

TABLE II. Final Anisotropic Thermal Parameters ($\times 10^4$) in the Form $\exp-(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})$ with Estimated Standard Deviations in Parentheses.

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ni	167.0(10)	16.3(1)	43.7(4)	0.7(3)	22.4(4)	0.8(2)
N(11)	145(6)	21(1)	49(3)	-6(2)	19(3)	1(1)
N(21)	153(6)	22(1)	46(2)	10(2)	23(3)	2(1)
N(1)	231(7)	19(1)	75(3)	-10(2)	43(3)	-4(1)
N(2)	249(7)	20(1)	64(3)	11(2)	48(3)	9(1)
C(11)	128(6)	28(1)	51(3)	-10(2)	26(3)	-4(1)
C(12)	150(7)	40(2)	53(3)	0(3)	17(4)	-1(2)
C(13)	175(8)	42(2)	57(3)	12(3)	18(4)	15(2)
C(14)	163(7)	26(1)	80(4)	5(2)	23(4)	11(2)
C(15)	162(7)	23(1)	54(3)	-2(2)	19(4)	0(1)
C(O1)	165(7)	26(1)	74(4)	-18(2)	37(4)	-13(2)
O(1)	301(7)	36(1)	71(3)	-19(2)	45(3)	-22(1)
C(1)	451(15)	19(1)	109(5)	-8(3)	90(7)	-10(2)
C(2)	384(13)	22(1)	103(5)	0(3)	68(6)	10(2)
C(3)	389(14)	21(1)	134(6)	-8(3)	50(7)	11(2)
C(O2)	195(8)	30(1)	52(3)	27(2)	45(4)	12(2)
O(2)	342(7)	39(1)	66(3)	-33(2)	59(3)	-22(1)
C(21)	137(7)	27(1)	53(3)	13(2)	30(3)	5(1)
C(22)	166(7)	43(2)	47(3)	10(3)	7(4)	-1(2)
C(23)	180(8)	38(2)	72(4)	-10(3)	11(4)	-13(2)
C(24)	181(8)	29(1)	72(3)	-1(2)	23(4)	-6(2)
C(25)	177(7)	23(1)	57(3)	2(2)	25(4)	-2(1)
O(W)	283(8)	28(1)	135(4)	-6(2)	20(4)	0(2)

TABLE III. Hydrogen Atom Parameters (coordinates: fractional $\times$ 10^3) with Estimated Standard Deviations in Parentheses.

	x	y	z	B (Å^2)
H(W1)	595(8)	49(3)	801(5)	5.0
H(W2)	441(7)	55(2)	701(4)	5.0
H(12)	-332(6)	246(2)	-157(4)	4.0
H(13)	-426(6)	369(2)	-140(4)	4.0
H(14)	-353(6)	418(2)	54(4)	4.0
H(15)	-156(6)	351(2)	222(4)	4.0
H(22)	386(6)	262(2)	660(4)	4.0
H(23)	457(6)	386(2)	632(4)	4.0
H(24)	374(6)	428(2)	436(4)	4.0
H(25)	184(6)	353(2)	270(4)	4.0
H(1a)	123(6)	41(2)	167(4)	4.0
H(1b)	-145(6)	32(2)	85(4)	4.0
H(2a)	111(6)	40(2)	455(4)	4.0
H(2b)	260(6)	34(2)	374(4)	4.0
H(3a)	-189(6)	45(2)	278(4)	4.0
H(3b)	-20(5)	-28(3)	268(3)	4.0

the hydrogen bonding to the lattice water molecule. The dimensions in the hydrogen bonding system are given in Table V(a) and the closest intermolecular contacts are listed in Table V(b).

The N_4-ligand coordinates to the nickel atom in an irregular square plane (Table VI, plane 1) with a tetrahedral twist of 15.9° (Fig. 3 and Table VI, planes 2 and 3) at the nickel atom. This twist is considerably greater than that found in related compounds (see Table VII) and results from steric effects imposed by the change from a 5-,5-,5- to a 5-,6-,5-membered chelate ring system. A comparison of structural data for these compounds is given in Table VII. In the present structure the N_{amide}–Ni–N_{amide} angle opens *ca.* 10° from that in the 5-,5-,5-system with a commensurate closing of the $N_{pyridine}$–Ni–$N_{pyridine}$ angle. A similar angular effect has been observed in the related [Cu(bppn)H_2O] complex [1, 2]. The average Ni–N_{amide} length of 1.864(4) Å is comparable with those in related compounds [4, 5] but the value for Ni–$N_{pyridine}$ of 1.912(3) Å is significantly shorter. However, this shortening is in accord with the observed closing of the $N_{pyridine}$–Ni–$N_{pyridine}$ angle towards the right angle of idealised square planar geometry.

The two picolinamide units are closely similar and if the central carbon atom, C(3), of the propane link is disregarded the molecular symmetry would be C_2 as shown in Fig. 3. The amide chelate rings show marked deviations from planarity (Table VI, planes 4 and 5); the amide nitrogen atoms show pyramidal distortions of 11.2 and 6.2° with smaller distortions of 2.9 and 3.8° for the amide carbon atoms (Table VI, planes 6–17). The enforced steric strain in the molecule further results in boat type distortions in the pyridyl rings (Table VI, planes 18 and 19) similar to those found in [Cu(6-mebpb)] [8]. The corresponding folding angles, γ and δ [8], are

TABLE IV. Bond Lengths and Angles with Estimated Standard Deviations in Parentheses.

(a) Distances (Å)

Ni–N(11)	1.911(2)	Ni–N(21)	1.914(2)
Ni–N(1)	1.861(3)	Ni–N(2)	1.867(3)
N(11)–C(11)	1.353(4)	N(21)–C(21)	1.346(4)
N(11)–C(15)	1.345(4)	N(21)–C(25)	1.344(4)
C(11)–C(12)	1.375(4)	C(21)–C(22)	1.370(4)
C(12)–C(13)	1.384(5)	C(22)–C(23)	1.382(5)
C(13)–C(14)	1.374(5)	C(23)–C(24)	1.374(5)
C(14)–C(15)	1.379(4)	C(24)–C(25)	1.386(4)
C(11)–C(O1)	1.494(4)	C(21)–C(O2)	1.499(4)
C(O1)–O(1)	1.249(4)	C(O2)–O(2)	1.249(4)
C(O1)–N(1)	1.329(4)	C(O2)–N(2)	1.325(4)
N(1)–C(1)	1.470(5)	N(2)–C(2)	1.463(4)
C(1)–C(3)	1.501(6)	C(2)–C(3)	1.459(6)
C(12)–H(12)	0.91(4)	C(22)–H(22)	0.89(4)
C(13)–H(13)	0.89(4)	C(23)–H(23)	0.93(4)
C(14)–H(14)	0.95(4)	C(24)–H(24)	0.97(4)
C(15)–H(15)	0.95(4)	C(25)–H(25)	0.97(4)
C(1)–H(1a)	1.08(4)	C(2)–H(2a)	0.95(4)
C(1)–H(1b)	0.96(4)	C(2)–H(2b)	1.13(4)
C(3)–H(3a)	1.16(4)	O(W)–H(W1)	0.78(5)
C(3)–H(3b)	1.06(5)	O(W)–H(W2)	0.85(4)

(b) Angles (°)

N(11)–Ni–N(1)	84.0(1)	N(21)–Ni–N(2)	83.8(1)
N(11)–Ni–N(21)	98.7(1)	N(1)–Ni–N(2)	96.0(1)
N(11)–Ni–N(2)	168.2(1)	N(21)–Ni–N(1)	167.7(1)
Ni–N(11)–C(11)	112.3(2)	Ni–N(21)–C(21)	112.8(2)
Ni–N(11)–C(15)	129.2(2)	Ni–N(21)–C(25)	128.9(2)
C(11)–N(11)–C(15)	118.5(3)	C(21)–N(21)–C(25)	118.2(3)
Ni–N(1)–C(O1)	115.9(2)	Ni–N(2)–C(O2)	115.8(2)
Ni–N(1)–C(1)	125.4(3)	Ni–N(2)–C(2)	128.1(3)
C(O1)–N(1)–C(1)	117.8(3)	C(O2)–N(2)–C(2)	115.9(3)
N(11)–C(11)–C(O1)	113.9(3)	N(21)–C(21)–C(O2)	113.4(3)
C(12)–C(11)–C(O1)	124.0(3)	C(22)–C(21)–C(O2)	124.0(3)
N(11)–C(11)–C(12)	121.9(3)	N(21)–C(21)–C(22)	122.4(3)
C(11)–C(12)–C(13)	119.2(3)	C(21)–C(22)–C(23)	119.2(3)
C(12)–C(13)–C(14)	119.0(3)	C(22)–C(23)–C(24)	118.7(3)
C(13)–C(14)–C(15)	119.4(3)	C(23)–C(24)–C(25)	119.4(3)
C(14)–C(15)–N(11)	121.9(3)	C(24)–C(25)–N(21)	121.8(3)
O(1)–C(O1)–C(11)	120.5(3)	O(2)–C(O2)–C(21)	120.1(2)
O(1)–C(O1)–N(1)	128.2(3)	O(2)–C(O2)–N(2)	128.0(2)
C(11)–C(O1)–N(1)	111.3(3)	C(21)–C(O2)–N(2)	111.8(3)
N(1)–C(1)–C(3)	110.6(3)	N(2)–C(2)–C(3)	113.4(3)
C(1)–C(3)–C(2)	116.5(4)		
C(11)–C(12)–H(12)	113(3)	C(21)–C(22)–H(22)	116(3)
C(13)–C(12)–H(12)	128(3)	C(23)–C(22)–H(22)	124(3)
C(12)–C(13)–H(13)	122(3)	C(22)–C(23)–H(23)	125(3)
C(14)–C(13)–H(13)	119(3)	C(24)–C(23)–H(23)	117(3)
C(13)–C(14)–H(14)	122(3)	C(23)–C(24)–H(24)	120(3)
C(15)–C(14)–H(14)	119(3)	C(25)–C(24)–H(24)	120(3)
N(11)–C(15)–H(15)	117(3)	N(21)–C(25)–H(25)	117(3)
C(14)–C(15)–H(15)	121(3)	C(24)–C(25)–H(25)	121(3)
N(1)–C(1)–H(1a)	111(2)	N(2)–C(2)–H(2a)	108(3)
N(1)–C(1)–H(1b)	103(3)	N(2)–C(2)–H(2b)	109(2)
C(3)–C(1)–H(1a)	97(2)	C(3)–C(2)–H(2a)	115(3)
C(3)–C(1)–H(1b)	108(3)	C(3)–C(2)–H(2b)	105(2)
H(1a)–C(1)–H(1b)	127(3)	H(2a)–C(2)–H(2b)	105(3)

(continued on facing page)

TABLE IV. *(continued)*

C(1)–C(3)–H(3a)	110(2)	C(2)–C(3)–H(3a)	106(2)
C(1)–C(3)–H(3b)	104(2)	C(2)–C(3)–H(3b)	107(2)
H(3a)–C(3)–H(3b)	102(4)	H(W1)–O(W)–H(W2)	113(3)

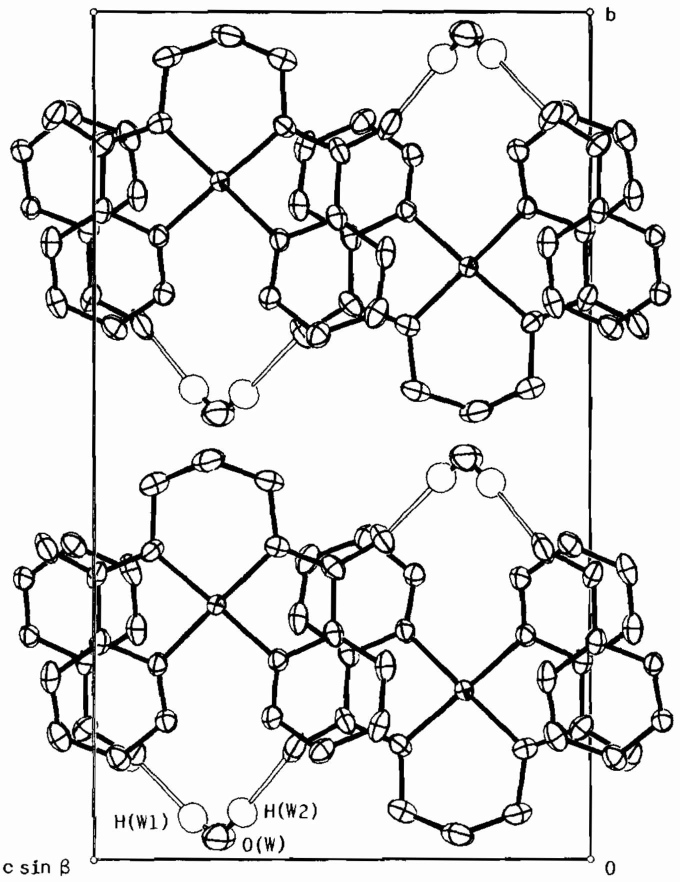

Fig. 2. The packing of the molecules in the unit cell showing the hydrogen bond network. The labelling of the water molecule also is included.

TABLE V[a]. Contact Distances (Å) with Estimated Standard Deviations in Parentheses.

(a) Proposed hydrogen bonds (angles in °)

	O$\cdots$O	H$\cdots$O	<O–H$\cdots$O
O(W)–H(W1)$\cdots\cdot$O(1^{I})	2.889(4)	2.12(5)	171(4)
O(W)–H(W2)$\cdots\cdot$O(2)	2.873(4)	2.03(4)	175(5)

(b) Intermolecular Distances <3.5 Å

O(2)$\cdots\cdot$C(25^{II})	3.171(4)	C(14)$\cdots\cdot$C(O2^{IV})	3.394(4)
C(11)$\cdots\cdot$C(21^{III})	3.282(4)	O(1)$\cdots\cdot$C(25^{III})	3.448(4)
C(15)$\cdots\cdot$O(1^{II})	3.357(4)	C(13)$\cdots\cdot$C(O2^{IV})	3.464(4)
C(14)$\cdots\cdot$O(2^{IV})	3.367(4)	C(O1)$\cdots\cdot$C(21^{III})	3.489(5)

[a] Roman numeral superscripts refer to the following equivalent positions relative to x, y, z: I $1 + x, y, 1 + z$; II $x, ½ - y, ½ + z$; III $x, ½ - y, z - ½$; IV $x - 1, ½ - y, z - ½$.

TABLE VI. Least-squares planes and their equations given by $lX' + mY' + nZ' - p = 0$ where X', Y' and Z' are orthogonal coordinates (Å) derived with respect to the orthogonal axes a', b, c. Deviations (Å) of relevant atoms from the planes are given in square brackets.

	l	m	n	p
Plane (1): N(1), N(2), N(11), N(21) [N(1) −0.20; N(2) 0.20; N(11) 0.19; N(21) −0.19; Ni 0.004]	−0.7964	−0.0075	0.6047	1.6009
Plane (2): Ni, N(11), N(21) [N(1) −0.39; N(2) 0.37]	−0.7098	−0.0007	0.7044	1.9323
Plane (3): Ni, N(1), N(2) [N(11) 0.39; N(21) −0.41]	−0.8757	−0.0151	0.4827	1.2101
Plane (4): N(11), C(11), C(O1), N(1) [N(11) −0.014; C(11) 0.023; C(O1) −0.023; N(1) 0.014; Ni −0.33; O(1) −0.04; C(1) 0.08]	−0.9026	−0.1825	0.3899	0.6433
Plane (5): N(21), C(21), C(O2), N(2) [N(21) 0.010; C(21) −0.018; C(O2) 0.018; N(2) −0.010; Ni 0.33 O(2) <0.001; C(2) −0.17]	−0.9083	0.1513	0.3899	1.2267
Plane (6): N(1), C(1), C(O1) [Ni −0.30]	−0.9143	−0.1389	0.3805	0.7529
Plane (7): N(1), C(1), Ni [C(O1) −0.24]	−0.8223	−0.1110	0.5581	1.0805
Plane (8): N(1), C(O1), Ni [C(1) −0.24]	−0.8963	0.0323	0.4423	1.2665
Plane (9): N(2), C(2), C(O2) [Ni 0.17]	−0.9073	0.0394	0.4186	1.0551
Plane (10): N(2), C(2), Ni [C(O2) 0.14]	−0.8538	0.0351	0.5194	1.5066
Plane (11): N(2), C(O2), Ni [C(2) 0.13]	−0.8892	−0.0519	0.4545	0.9901
Plane (12): C(O1), O(1), C(11) [N(1) 0.06]	−0.8953	−0.2131	0.3911	0.5250
Plane (13): C(O1), O(1), N(1) [C(11) 0.07]	−0.9143	−0.1677	0.3686	0.6625
Plane (14): C(O1), C(11), N(1) [O(1) 0.05]	−0.9125	−0.2136	0.3489	0.5161
Plane (15): C(O2), O(2), C(21) [N(2) −0.08]	−0.8931	0.1753	0.4143	1.4656
Plane (16): C(O2), O(2), N(2) [C(21) −0.09]	−0.9153	0.1123	0.3868	1.0995
Plane (17): C(O2), C(21), N(2) [O(2) −0.07]	−0.9175	0.1731	0.3581	1.1315
Plane (18): N(11), C(11)–(15) [N(11) 0.024; C(11) −0.024; C(12) 0.002; C(13) 0.018; C(14) −0.016; C(15) −0.006; Ni 0.03; C(O1) −0.23]	0.8333	0.3440	−0.4328	0.1221
Plane (19): N(21), C(21)–(25) [N(21) 0.031; C(21) −0.029; C(22) 0.001; C(23) 0.024; C(24) −0.021; C(25) −0.007; Ni 0.04; C(O2) −0.26]	−0.8497	0.3276	0.4132	2.2463
Plane (20): N(11), C(11), C(15) [Ni −0.11]	0.7992	0.3682	−0.4751	0.2192
Plane (21): C(12), C(13), C(14)	0.8527	0.3308	−0.4044	0.0102
Plane (22): N(11), C(11)–(13) [N(11) 0.006; C(11) −0.012; C(12) 0.012; C(13) −0.006; C(14) −0.07; C(15) −0.06]	0.8337	0.3214	−0.4490	0.0003
Plane (23): N(11), C(13)–(15) [N(11) −0.001; C(13) 0.001; C(14) −0.002; C(15) 0.002; C(11) −0.08; C(12) −0.05]	0.8310	0.3678	−0.4174	0.2965
Plane (24): N(21), C(21), C(25) [Ni −0.12]	−0.8098	0.3605	0.4630	2.6826
Plane (25): C(22), C(23), C(24)	−0.8740	0.3069	0.3768	1.8649

(continued on facing page)

TABLE VI. *(continued)*

	l	*m*	*n*	*p*
Plane (26): N(21), C(21)–(23) [N(21) 0.007; C(21) –0.014; C(22) 0.014; C(23) –0.007; C(24) –0.09; C(25) –0.07]	–0.8492	0.2999	0.4347	2.2165
Plane (27): N(21), C(23)–(25) [N(21) –0.002; C(23) 0.002; C(24) –0.004; C(25) 0.004; C(21) –0.10; C(22) –0.07]	–0.8480	0.3562	0.3924	2.3439
Plane (28): N(1), N(2), C(1), C(2) [N(1) 0.059; N(2) –0.059; C(1) –0.065; C(2) 0.065; Ni –0.04; C(3) 0.63]	–0.8941	–0.0459	0.4455	1.0221

Dihedral Angles (°)

2–3	15.9	6–7	11.6	12–13	3.1
20–21	5.5	6–8	10.5	12–14	2.6
22–23	3.2	7–8	11.4	13–14	2.9
24–25	6.9	9–10	6.5	15–16	4.1
26–27	4.0	9–11	5.7	15–17	3.5
		10–11	6.5	16–17	3.9

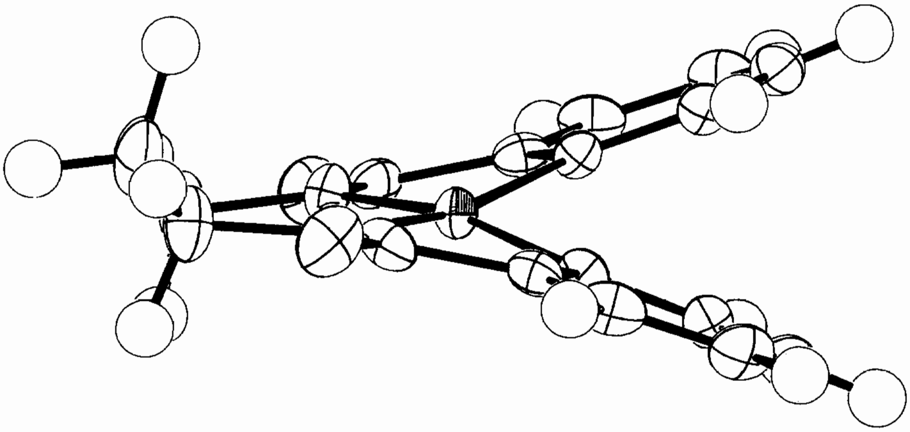

Fig. 3. The [Ni(bppn)] molecule oriented to show the tetrahedral twist at the nickel atom and the approximate two-fold relationship between the picolinamide units.

TABLE VII. Comparison of Structural Data for Complexes Closely Related to Ni(bppn). Distances in Å and angles in degrees.

	Ni(bppn)	Ni(bpen)	Ni(bpch)
$\mathrm{Ni{-}N}_{pyridine}$	1.912(3)	1.952(6)	1.944(8)
$\mathrm{Ni{-}N}_{amide}$	1.864(4)	1.839(6)	1.868(7)
H(5)····H(5′)	2.30	1.81	2.17
$\mathrm{N}_{pyridine}\mathrm{{-}Ni{-}N}_{pyridine}$	98.7(1)	108.4(3)	107.0(4)
$\mathrm{N}_{amide}\mathrm{{-}Ni{-}N}_{amide}$	96.0(1)	82.9(3)	86.2(4)
Tetrahedral Twist	15.9	1.5	5.7

(continued overleaf)

TABLE VII. *(continued)*

	Ni(bppn)	Ni(bpen)	Ni(bpch)
Pyramidal Distortions (°)			
N_{amide}	11.2, 6.2	2.6	30.8
C_{amide}	2.9, 3.8	1.2	1.6
Reference	this work	4	5

5.5 and 3.2° for ring 1 and 6.9 and 4.0° for ring 2 (Tables VI, planes 20–27). This distortion is not as large as that observed in the α- and β-forms of [Cu(bppn)H_2O] [1, 2]. The tetrahedral twist at the nickel atom and the approximate two-fold relationship between the two picolinamide units causes the central six-membered chelate ring to adopt a skewed conformation intermediate between that of a boat and a chair (Table VI, plane 28); the relevant torsion angles about C(1)–N(1) and C(2)–N(2) are –39.0 and 18.2° respectively. The presence of the central six-membered chelate ring clearly demonstrates here the severe 'B-strain' effect resulting from planar coordination of a tetradentate ligand of this geometry [3].

Acknowledgements

We thank Mr. D. C. Craig of the School of Chemistry, University of New South Wales for his assistance with the collection of intensities and that School for the use of their diffractometer.

References

1 F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 57,* 43 (1982).
2 F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 90,* 25 (1984).
3 J. G. Gibson and E. D. McKenzie, *J. Chem. Soc. (A),* 1666 (1971).
4 F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 57,* 9 (1982).
5 M. Mulqi, F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 52,* 73 (1981).
6 'International Tables for X-Ray Crystallography', Vol. IV, Kynoch Press, Birmingham, pp. 72–79 (1974).
7 C. K. Johnson, ORTEP, Report ORNL-3794 (1965), Revised 1971, Oak Ridge National Laboratory, Tennessee, U.S.A.
8 R. L. Chapman, F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 52,* 169 (1981).