Inorganica Chimica Acta, 57 (1982) 9–13

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

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Received May 14, 1981

*[N,N'-Bis(2'-pyridinecarboxamido)-1,2-ethane]nickel(II) monohydrate, $C_{14}H_{14}N_4O_3Ni$, is monoclinic, space group I2/a, with a = 7.241(3), b = 17.141(6), c = 11.132(3) Å, β= 102.2(1)°, Z = 4. The structure was refined to R = 0.071 for 949 photographic reflexions by least-squares calculations. The molecules have space group imposed C2(2) symmetry. The nickel atom is four coordinate with the ligand acting as a planar N_4-tetradentae [Ni–N(*amide*) 1.839(6), Ni–N(*pyridine*) 1.952(6) Å, N(*amide*)–Ni–N(*amide*) 82.9(3)°, N(*pyridine*)–Ni–N(*pyridine*) 108.4(3)°]. The amide nitrogen atom is almost trigonally planar, and that the ligand can adopt a nearly planar arrangement about the nickel atom is due to the flexible ethylene link. The chelate molecules stack with their molecular planes parallel to (10$\bar{1}$). The water molecule hydrogen bonds the carboxyl oxygen atoms of two chelate molecules which are related by the two-fold axis contained by it.*

Introduction

The ligand N,N'-bis(2'-pyridinecarboxamide)-1,2-ethane ($bpenH_2$) forms deprotonated complexes in which it acts as an essentially planar N_4-tetradentate [1]. The formation of N_4-planar coordination about a metal atom causes steric strain in the ligand due to close 6'-pyridyl hydrogen atom contacts. The structures of the copper(II) complex [2] and the copper(II) complexes of analogous ligands [3, 4] show that this strain can be minimised by an out-of-plane movement of the copper atom on the formation of a square-based pyramidal stereochemistry together with distortions within the ligands. Nickel(II) forms a square-planar diamagnetic complex analogous to that formed with N,N'-bis(2'-pyridinecarboxamide)-1,2-cyclohexane [5]. In the crystal structure of the latter [6] distortions within the ligand, particularly at the amide nitrogen atoms, and a small tetrahedral twist at the nickel atom are evident. We here report the crystal structure analysis of the nickel complex, $Ni(bpen)H_2O$.

Experimental

Crystal Data

$C_{14}H_{14}N_4O_3Ni$, M_r = 345.0, Monoclinic, a = 7.241(3), b =17.141(6), c = 11.132(3) Å, β= 102.2(1)°, U = 1350.5 Å^3, Z = 4, D_c = 1.697 Mg m^{-3}, F(000) = 712, μ(Mo-K_α) = 1.46 mm^{-1}, μ(Cu-K_α) = 2.12 mm^{-1}. Systematic absences: hkl if $h + k + l \neq 2n$ and $h0l$ if $h(l) \neq 2n$, space group Ia (non-std. No. 9) or $I2/a$ (non-std., No. 15).

The complex crystallises as yellow needles with the needle axis parallel to b. Cell parameters were determined from precession photographs using Mo-K_α radiation. Intensities were estimated visually from precession photographs for the layers 0–2kl and hk0–2 using Mo-K_α radiation and from equi-inclination Weissenberg photographs for the layers h0–7l using Cu-K_α radiation. They were corrected for Lorentz and polarisation effects but not for absorption or extinction. The structure factors were placed on a common scale by internal correlation and 949 non-zero unique reflexions were obtained. Scattering factors were taken from 'International Tables for X-Ray Crystallography' [7]. All calculations were carried out on a UNIVAC 1106 computer with programmes written by F.S.S.

A statistical analysis of the intensity data [8] gives an average value of 0.63 for M [= $\langle|F|^2/|F|^2\rangle$] and this together with the three dimensional Patterson synthesis indicates the space group to be centric. With only four formula units per cell each molecule must possess a centre of symmetry or a two-fold axis, only the latter is chemically feasible for the

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*Part XI: M. Mulqi, F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 52,* 177 (1981).

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

	x	y	z
Ni	2500	373.5(8)	0
N(11)	1438(9)	−293(4)	−1398(5)
N	1643(9)	1177(4)	−1066(5)
C(11)	586(10)	129(5)	−2404(6)
C(12)	−275(12)	−198(6)	−3466(6)
C(13)	−283(13)	−1002(6)	−3603(7)
C(14)	565(14)	−1440(6)	−2611(8)
C(15)	1411(14)	−1079(6)	−1534(7)
C(O)	766(11)	1003(5)	−2197(6)
C	1881(12)	1976(5)	−627(7)
O	95(9)	1469(4)	−3042(5)
O(W)	−2500	2249(5)	−5000

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 given in Parentheses.

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ni	168(3)	22(1)	47(1)	0	9(1)	0
N(11)	159(12)	29(2)	46(4)	2(6)	20(6)	0(3)
N	184(14)	22(2)	55(4)	7(6)	−3(7)	7(3)
C(11)	148(15)	33(3)	41(5)	−3(7)	21(7)	2(3)
C(12)	165(16)	52(5)	44(5)	7(9)	17(7)	2(4)
C(13)	207(20)	54(5)	65(6)	−1(10)	4(9)	−22(5)
C(14)	260(22)	37(4)	74(7)	9(9)	0(10)	−14(4)
C(15)	235(21)	39(4)	68(6)	−7(9)	−1(10)	−2(4)
C(O)	171(16)	35(3)	50(5)	−3(8)	13(8)	1(3)
C	206(19)	25(3)	77(7)	15(7)	−9(10)	4(4)
O	248(15)	45(3)	73(5)	32(6)	−5(7)	16(3)
O(W1)	192(17)	38(3)	69(6)	0	−3(9)	0

complex molecule. The structure was solved by the heavy-atom method and refined by least-squares in which $\Sigma w\Delta^2$ was minimised. Weights were initially unity and in the final stages $w = (5.0 + 0.05|F_o| + 0.001|F_o|^2)^{-1}$. The positions of the hydrogen atoms were calculated, assuming appropriate geometries and C–H and O–H to be 1.0 and 0.9Å respectively, and their contribution to the structure factors included but at no time were their parameters refined. Refinement was terminated when the maximum shift in any parameter was $<0.1\ \sigma$. The final value for R was 0.071 and for R' $[=(\Sigma w\Delta^2/\Sigma w|F_o|^2)^{1/2}]$ was 0.092. A final difference map showed no densities $>|0.7|$ eÅ^{-3}. The final atomic parameters are given in Tables I, II and III. A list of observed and calculated structure factors has been deposited with the Editor.

TABLE III. Hydrogen Atom Parameters (coordinates: fractional $\times 10^3$).[a]

	x	y	z
H(12)	−93	13	−417
H(13)	−88	−126	−440
H(14)	56	−202	−266
H(15)	203	−141	−82
H(1)	245	229	−121
H(2)	61	221	−62
H(W)	−169	201	−439

[a] For all H atoms $B = 5.0$ Å^2.

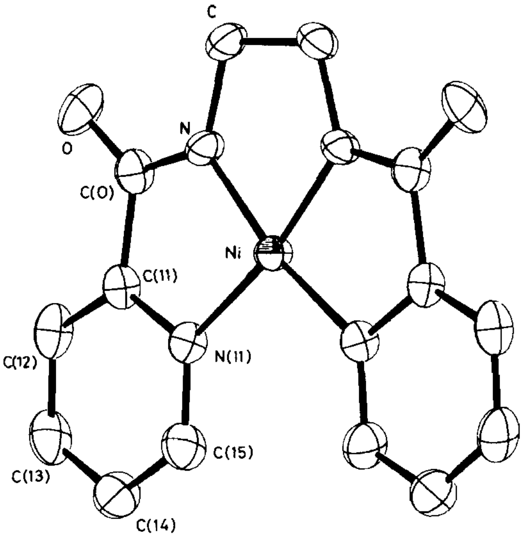

Fig. 1. A perspective drawing of the [Ni(bpen)] molecule together with the atom labelling. Thermal ellipsoids are drawn to include 35% probability.

Discussion

Figure 1 gives a perspective drawing [9] of the chelate molecule and the labelling of the atoms. The packing of the molecules in the unit cell is shown in Fig. 2. Both the chelate molecule and the lattice water molecule have space group imposed $C2(2)$ symmetry. The chelate molecules stack with their molecular planes parallel to $(10\bar{1})$. The water molecule hydrogen bonds (O(W)H(W)····O 2.887(7) Å) the carboxyl oxygen atoms of two chelate molecules which are related by the two-fold axis contained by it. The closest non-bonded contacts are between molecules related by the a-glide plane [C(14)···O$^{\mathrm{I}}$ 3.41(1), N(11)···C(12$^{\mathrm{I}}$) 3.43(1) and C(11)···C(12$^{\mathrm{I}}$) 3.45(1) Å where the superscript I refers to the position ½ + x, $-y$, z relative to x, y, z] and all other contacts are >3.5 Å.

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

a) Distances (Å)*			
Ni–N(11)	1.952(6)	Ni–N	1.839(6)
N(11)–C(15)	1.357(10)	N–C	1.452(10)
N(11)–C(11)	1.366(9)	N–C(O)	1.319(9)
C(11)–C(12)	1.337(10)	C(O)–O	1.251(9)
C(12)–C(13)	1.386(13)	C(O)–C(11)	1.517(11)
C(13)–C(14)	1.369(13)	C–C′	1.491(16)
C(14)–C(15)	1.373(11)		
b) Angles (°)*			
N(11)–Ni–N	84.3(3)	N(11)–Ni–N′	167.3(3)
N(11)–Ni–N(11′)	108.4(3)	N–Ni–N′	82.9(3)
Ni–N(11)–C(11)	112.2(5)	Ni–N–C(O)	118.4(6)
Ni–N(11)–C(15)	131.6(5)	Ni–N–C	119.3(5)
C(11)–N(11)–C(15)	116.2(6)	C(O)–N–C	122.3(6)
N(11)–C(11)–C(12)	123.2(8)	C(11)–C(12)–C(13)	120.3(8)
N(11)–C(11)–C(O)	112.9(6)	C(12)–C(13)–C(14)	117.8(7)
C(12)–C(11)–C(O)	123.9(7)	C(13)–C(14)–C(15)	119.9(9)
C(11)–C(O)–O	127.2(8)	C(14)–C(15)–N(11)	122.6(8)
C(11)–C(O)–N	112.1(7)	N–C–C′	108.7(6)
O–C(O)–N	120.6(7)		

*Atoms marked with a prime are related to those at x, y, z by the two-fold axis at ¼, y, 0.

TABLE V. 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 are given in Square Brackets. (For prime notation see footnote Table IV).

	l	m	n	p
Plane (1): N(11), N, N(11′), N′ [N(11) 0.016; N –0.020]	0.8754	0.0000	–0.4833	1.7339
Plane (2): Ni, N(11), N(11′)	0.8802	0.0000	–0.4747	1.7389
Plane (3): Ni, N, N′	0.8672	0.0000	–0.4979	1.7249
Plane (4): N(11), C(11)–C(15) [N(11) –0.003; C(11) 0.008; C(12) –0.009; C(13) 0.006; C(14) –0.001; C(15) <|0.001|; Ni –0.01; C(O) 0.08]	0.8617	0.0413	–0.5058	1.7575
Plane (5): Ni, N(11), C(11), C(O), N [Ni –0.006; N(11) 0.014; C(11) –0.017; C(O) 0.009; N –0.001; O 0.02]	0.8704	0.0099	–0.4922	1.7411
Plane (6): N, C, C′, N′ [N 0.036; C –0.058]	0.8523	0.0000	–0.5231	1.7081
Plane (7): N, C(O), C [Ni –0.07]	0.8675	0.0572	–0.4942	1.8352
Plane (8): N, C(O), Ni [C –0.06]	0.8740	0.0122	–0.4859	1.7400
Plane (9): N, C, Ni [C(O) –0.05]	0.8891	0.0418	–0.4559	1.7742
Plane (10): C(O), O, C(11) [N –0.02]	0.8672	–0.0065	–0.4979	1.7351

(continued overleaf)

TABLE V. *(continued)*

	l	*m*	*n*	*p*
Plane (11): C(O), O, N [C(11) −0.03]	0.8742	0.0106	−0.4855	1.7365
Plane (12): C(O), C(11), N [O −0.02]	0.8764	−0.0095	−0.4815	1.6929

Dihedral angles (°)

1–4	2.8	7–8	2.7	10–11	1.3
1–5	0.8	7–9	2.7	10–12	1.1
4–5	2.0	8–9	2.6	11–12	1.2
2–3	1.5				

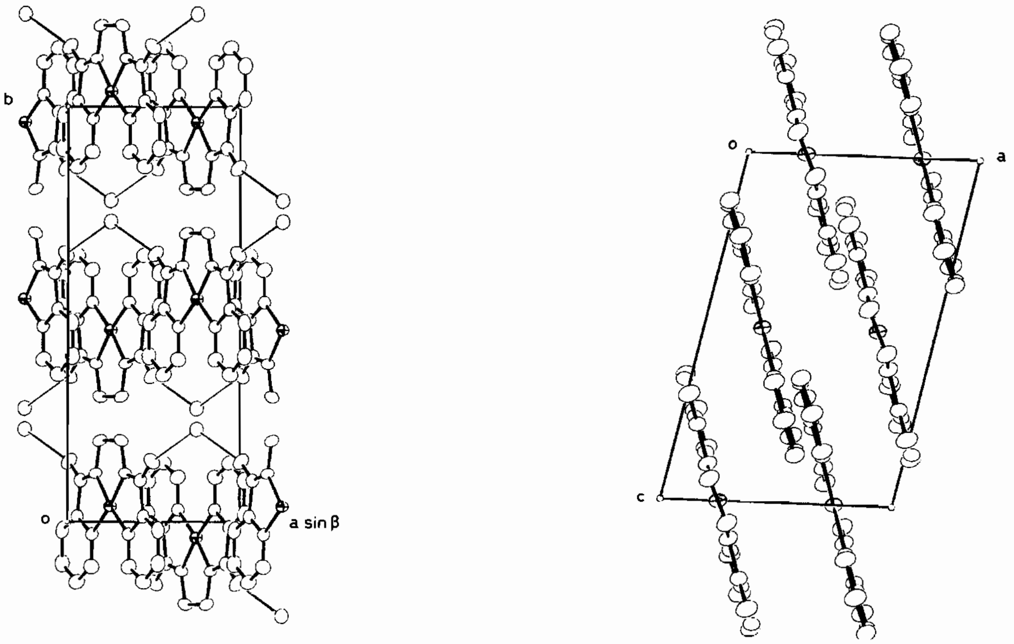

Fig. 2. The packing of the molecules in the unit cell. a) Projected down *c* with hydrogen bonding represented by thin lines. b) Projected down *b* with the hydrogen-bonding and lattice water molecule omitted for clarity.

The bond lengths and angles are given in Table IV. The N_4-ligand coordinates to the nickel atom in an irregular square plane (Table V, plane 1) with a small tetrahedral twist of 1.5° at the nickel atom (Table V, planes 2 and 3). The five-membered amide chelate ring and the pyridine ring are each planar (Table V, planes 4 and 5) with a dihedral angle of 2.0° between them. The other chelate ring containing the ethylene link is almost planar (Table V, plane 6) giving rise to a closely eclipsed conformation. The dihedral angles between the pyridine ring and the N_4-plane and its symmetry related ring are 2.8 and 4.7° respectively. This orientation gives rise to a rather close H(15)···H(15′) contact of 1.81 Å for the hydrogen atoms in the 6-positions of the pyridine ring. This distance is considerably smaller than the corresponding distance of 1.98 Å in [Cu(bpb)H_2O] [3], which has a much less flexible central benzene link, and of 2.24 and 2.27 Å in the analogous copper complex [Cu(bpen)H_2O]H_2O [2]. The closeness of this contact is in accord with the trend noted from proton n.m.r. studies [1].

The carboxyl carbon atom has the expected trigonal-planar geometry (Table V, planes 10–12) and the amide nitrogen atom has a small but significant pyramidal distortion, the average value for the dihedral angles between the relevant three atom planes (Table V, planes 7–9) being 2.6°. This arrangement of the ligand markedly contrasts with that found in Ni(bpch) [6] in which the only change in the ligand is the replacement of the ethylene link by that of 1,2-cyclohexane. In this latter structure the amide nitrogen atoms have a geometry intermediate between trigonal-planar and pyramidal and there is twisting of both the non-planar amide chelate ring and the pyridine ring relative to each other and also relative to the N_4-plane. These rotations result in a much greater H(15)···H(15') contact of 2.17 Å [6]. That the bpen ligand is able to adopt a more planar arrangement about the nickel atom is clearly due to the greater rotational freedom of the ethylene link. In the structure of the 1,2-cyclohexane analogue the amide nitrogen atoms are in a *gauche* conformation (torsion angle about C(1)–C(1') of 39°) as compared with the closely eclipsed conformation in the present structure (torsion angle of 11°).

The Ni–N(*amide*) distance of 1.839(6) Å is, as expected, shorter than the Ni–N(*pyridine*) distance of 1.952(6) Å. The former distance is significantly shorter ($\Delta l/\sigma(\Delta l) = 3.1$ [10]) than that of 1.868(7) Å in Ni(bpch) [6] and this is a reflection of the closer planarity of the amide nitrogen atom in the present structure. In combination with this planarity the nearly eclipsed ethylene conformation leads to a smaller N(*amide*)–Ni–N(*amide*) angle of 82.9(3)° compared with that of 96.2(3)° in Ni(bpch) [6] whilst the N(*pyridine*)–Ni–N(*pyridine*) angle of 108.4(3)° remains virtually unchanged.

The most strking aspect of the structure is the planar nature of the complex molecule as a whole, and in particular the planarity of the N-*amide* atoms and of the NiN_4 chromophore. This is allowed by the acceptance of both an eclipsed conformation of the ethylene C–H bonds and the shortest pyridyl hydrogen–hydrogen contact observed thus far.

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