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Studies on the Metal–Amide Bond.
VIII*. The Crystal Structure of [N,N′-bis(2′-pyridinecarboxamido)-*trans*-1,2-cyclohexane] nickel(II)

MOH'D MULQI, FREDERICK S. STEPHENS and ROBERT S. VAGG

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

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*[N,N′-bis(2′-pyridinecarboxamido)-*trans*-1,2-cyclohexane] nickel(II) $C_{18}H_{18}N_4O_2Ni$, is monoclinic, space group* I2/a, *with* a = *13.652(8),* b = *12.127(6),* c = *10.739(5) Å, β = 106.0(1)°,* Z = *4. The structure was refined to* R = *0.088 for 811 photographic reflexions using least-squares calculations. The molecule has space group imposed C2(2) symmetry and the nickel atom is four-coordinate with the ligand acting as a distorted square-planar N_4-tetradentate [Ni–N(*amide*) 1.868(7), Ni–N(*pyridine*) 1.944(8) Å, N(amide)–Ni–N(*amide) 86.2(4)°, *N(*pyridine*)–Ni–N(*pyridine*) 107.0(4)°]. The amide nitrogen atom is best described as having a flattened pyramidal geometry. Steric interactions are further alleviated by rotations within the non-planar amide chelate ring. The cyclohexane ring adopts a skew-chair conformation in which the methine hydrogens are in* trans*-configuration. The molecules are packed in the lattice in layers parallel to (101).*

Introduction

The ligand N,N′-bis(2′-pyridinecarboxamide)-1,2-cyclohexane, ($bpchH_2$), has been characterized in its interaction with transition metal ions [1]. The crystal structure of two isomeric forms of the deprotonated copper complex, [Cu(*trans*-bpch)H_2O]H_2O, and [Cu(*cis*-bpch)H_2O]H_2O, have been reported [2, 3]. In both structures the copper is five-coordinate with the N_4-ligand encompassing the base of a distorted square-based pyramid. The reaction of the ligand with bivalent nickel in alkaline solution yields a diamagnetic solid whose magnetic and spectral properties are consistent with square-planar coordination [1]. The analysis of the crystal structure of this complex, [Ni(*trans*-bpch)], is described below.

Experimental

The complex was prepared as described previously [1]. Recrystallization from ethanol yielded red-orange needles elongated along [001]. X-ray studies of a significant number of the crystals indicate that unlike the analogous copper complex only one crystalline species exists.

Crystal Data

$C_{18}H_{18}N_4O_2Ni$, M_r = 381.1, Monoclinic, a = 13.652(8), b = 12.127(6), c = 10.739(5) Å, β = 106.0(1)°, U = 1709.1 Å^3, D_m = 1.50 (by flotation), Z = 4, D_c = 1.481 Mg m^{-3}, $F(000)$ = 776, μ(Cu-K_α) = 1.74 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).

Cell parameters were determined from Weissenberg photographs using Cu-K_α radiation. 1088 non-zero reflexions were recorded on layers h0-5l and hk0-4 from equi-inclination Weissenberg photographs using Cu-k_α radiation. Intensities were estimated visually and corrected for Lorentz and polarisation effects but not for absorption or extinction. The observed structure factors were placed on a common scale by internal correlation generating a unique data set of 811 reflexions. Scattering factor curves were taken from 'International Tables for X-Ray Crystallography' [4]. All calculations were carried out on a UNIVAC 1106 computer using programmes written by F.S.S.

Structure Determination

A statistical analysis of the intensity data gives an average of 0.73 for M (=$\langle|F|^2/|F|^2\rangle$) [5] and this together with the three dimensional Patterson synthesis indicates the space group to be centric. Since the cell contains four formula units the molecule must possess either a centre of symmetry or a two-fold axis; only the latter is chemically feasible. The structure was solved by the heavy atom method. Refinement was by full-matrix least-squares calcula-

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*Part VII: D. J. Barnes, R. L. Chapman, F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta. 51,* 155 (1981).

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

	x	y	z
Ni	2500	1684(2)	0
O	1312(6)	265(6)	2540(7)
N(11)	1665(6)	2638(7)	744(8)
N(1)	1890(6)	559(6)	712(8)
C(11)	1265(7)	2108(9)	1615(9)
C(12)	674(7)	2580(10)	2306(11)
C(13)	458(8)	3722(10)	2135(11)
C(14)	853(8)	4279(8)	1287(12)
C(15)	1431(8)	3754(9)	561(10)
C(1)	2327(8)	−570(9)	641(11)
C(2)	1621(10)	−1561(9)	623(12)
C(3)	2283(12)	−2656(9)	584(13)
C(O)	1498(7)	850(8)	1697(10)

tions in which the function minimized was $\Sigma w\Delta^2$. Initially a weight, w, of unity was given for each reflexion, but in the final cycles $w = (0.25 + 1.25|F_o| + 0.0025|F_o|^2)^{-1}$ was used. After isotropic refinement a difference map yielded the approximate positions of the hydrogen atoms; these positions were optimised assuming C–H to be 1.0 Å. They were included in subsequent calculations but their parameters were not refined. Refinement was continued with anisotropic thermal parameters for all non-hydrogen atoms and terminated when the maximum shift in any parameter was $<0.01\ \sigma$. The final value for R was 0.088 and for $R'[=(\Sigma w\Delta^2/\Sigma|F_o|^2)^{1/2}]$ was 0.131. A final difference map showed no electron density $>|0.8|$ 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 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	82(2)	78(2)	109(3)	0	42(2)	0
O	98(6)	80(6)	95(9)	−21(5)	55(6)	1(7)
N(11)	64(5)	60(6)	82(10)	5(5)	32(6)	8(7)
N(1)	71(6)	47(5)	75(9)	−3(4)	44(6)	5(7)
C(11)	44(5)	90(8)	77(10)	−2(6)	18(7)	20(10)
C(12)	58(7)	104(10)	83(12)	10(7)	36(7)	−6(9)
C(13)	63(7)	82(8)	108(13)	2(7)	30(8)	−1(11)
C(14)	73(7)	62(8)	110(13)	14(6)	24(9)	−37(9)
C(15)	63(7)	75(8)	88(11)	13(6)	24(8)	2(10)
C(1)	73(7)	76(8)	92(14)	1(6)	27(8)	4(9)
C(2)	104(9)	74(9)	110(13)	−15(7)	49(9)	−4(10)
C(3)	151(12)	59(9)	122(16)	−15(8)	65(12)	5(10)
C(O)	50(6)	60(7)	80(11)	−15(5)	27(7)	−24(9)

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

	x	y	z
H(12)	39	318	292
H(13)	5	413	265
H(14)	75	509	113
H(15)	169	415	−8
H(1)	295	−65	138
H(21)	109	−146	−20
H(22)	135	−155	140
H(31)	181	−329	64
H(32)	282	−267	142

[a] For all hydrogen atoms $B = 6.0$ Å^2.

Discussion

Bond lengths and angles in the molecule are listed in Table IV. Figure 1 shows a perspective drawing of the molecule with atom labelling [6]. The molecule has space group imposed $C2(2)$ symmetry. The packing of the molecules in the cell is shown in Fig. 2. The chelate molecules pack in layers parallel to (101) in which the closest non-bonded contact is between atoms from parallel molecules (C(13)····O at $-x$, ½ + y, ½ − z 3.15(1) Å). All other intermolecular contacts are >3.35 Å.

The ligand bonds to the nickel atom via the two pyridyl and the two amide nitrogen atoms in an

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

Distances (A)^a			
Ni–N(11)	1.944(8)	Ni–N(1)	1.868(7)
N(11)–C(11)	1.366(13)	N(11)–C(15)	1.393(14)
C(11)–C(12)	1.363(14)	C(11)–C(O)	1.556(14)
C(12)–C(13)	1.417(16)	C(13)–C(14)	1.358(16)
C(14)–C(15)	1.405(14)	C(O)–O	1.231(12)
N(1)–C(O)	1.504(13)	N(1)–C(1)	1.357(12)
C(1)–C(2)	1.537(16)	C(1)–C(1′)	1.574(18)
C(2)–C(3)	1.613(17)	C(3)–C(3′)	1.527(21)
Angles (°)^a			
N(11)–Ni–N(1)	83.6(3)	N(11)–Ni–N(1′)	168.7(3)
N(11)–Ni–N(11′)	107.0(4)	N(1)–Ni–N(1′)	86.2(4)
Ni–N(11)–C(11)	113.1(7)	Ni–N(1)–C(1)	114.7(6)
Ni–N(11)–C(15)	131.2(15)	Ni–N(1)–C(O)	116.4(6)
C(11)–N(11)–C(15)	115.7(9)	C(1)–N(1)–C(O)	121.5(8)
N(11)–C(11)–C(12)	125.7(8)	N(11)–C(11)–C(O)	112.6(6)
C(12)–C(11)–C(O)	121.6(9)	C(11)–C(12)–C(13)	118.2(10)
C(12)–C(13)–C(14)	117.7(10)	C(13)–C(14)–C(15)	122.3(10)
N(11)–C(15)–C(14)	120.3(10)	N(1)–C(O)–C(11)	109.3(9)
N(1)–C(O)–O	129.0(9)	C(11)–C(O)–O	121.7(9)
N(1)–C(1)–C(2)	117.2(9)	N(1)–C(1)–C(1′)	105.3(10)
C(2)–C(1)–C(1′)	109.1(9)	C(1)–C(2)–C(3)	106.9(10)
C(2)–C(3)–C(3′)	111.6(10)		

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

TABLE V. Least-squares Planes Data.

(a) Least-square planes and their equations given by $lX' + mY' + nZ' - p = O$, where X', Y' and Z' are orthogonal coordinates related to the atomic coordinates X, Y and Z by $X' = X \sin\beta$, $Y' = Y$ and $Z' = Z + X \cos\beta$. Deviations (A) of relevant atoms from the planes are given in square brackets. Atoms marked with a prime are related to those at *x, y, z* by the two-fold axis at ¼, *y*, O.

	l	*m*	*n*	*p*
Plane (1): N(11), N(1), N(1′), N(11′) [N(11) –0.062; N(1) 0.076]	0.7399	0.0000	0.6727	1.7945
Plane (2): N(11), Ni, N(11′)	0.7125	0.0000	0.7017	1.6773
Plane (3): N(1), Ni, N(1′)	0.7788	0.0000	0.6272	1.9651
Plane (4): N(11), C(11)–(15) [N(11) 0.007; C(11) 0.006; C(12) –0.008; C(13) –0.002; C(14) 0.014; C(15) –0.017; Ni 0.08; C(O) –0.06]	0.8253	0.2121	0.5234	2.5649
Plane (5): N(11), C(11), C(O), N(1) [N(11) 0.033; C(11) –0.053; C(O) 0.053; N(1) –0.032; Ni 0.42; O 0.16]	0.9000	0.1114	0.4215	2.3623
Plane (6): C(1), C(3), C(3′) C(1′) [C(1) 0.034; C(3) –0.035; C(2) –0.76]	0.9439	0.0000	0.3302	2.7861
Plane (7): C(1), C(2), C(3)	0.2851	–0.0235	0.9582	0.7071
Plane (8): C(11), N(11), C(O) [C(12) –0.07]	0.8445	0.1696	0.5080	2.4747

(continued overleaf)

TABLE V. *(continued)*

	l	*m*	*n*	*p*
Plane (9): C(11), C(12), C(O) [N(11) –0.07]	0.8138	0.1634	0.5577	2.4705
Plane (10): C(O), N(1), C(11) [O –0.03]	0.9223	0.1852	0.3392	2.4314
Plane (11): C(O), N(1), O [C(11) –0.04]	0.9241	0.1588	0.3477	2.4183
Plane (12): C(O), C(11), O [N(1) –0.03]	0.9136	0.1834	0.3630	2.4423
Plane (13): N(1), Ni, C(O) [C(1) 0.67]	0.8788	–0.1998	0.4334	2.0673
Plane (14): N(1), Ni, C(1) [C(O) 0.60]	0.6615	0.1475	0.7353	1.7798
Plane (15): N(1), C(O), C(1) [Ni 0.88]	0.9003	0.3256	0.2887	2.4695

(b) Dihedral angles (°) between relevant planes.

2–3	5.7	10–11	1.6	13–10	23.0
1–4	15.7	10–12	1.5	13–11	21.4
1–5	18.3	11–12	1.8	10–8	10.3
4–5	9.3			10–9	13.6
		13–14	29.5		
6–7	54.2	13–15	31.7		
		14–15	31.1		

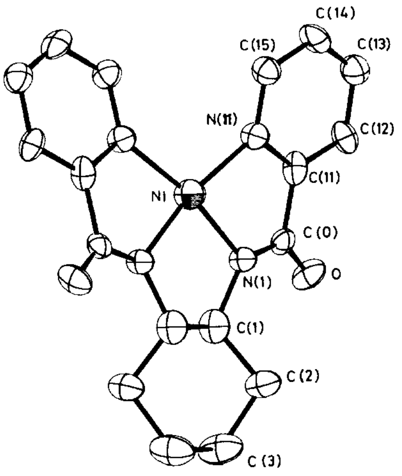

Fig. 1. Perspective drawing of the molecule showing the labelling of the atoms. Thermal ellipsoids for the atoms are scaled to include 35% probability.

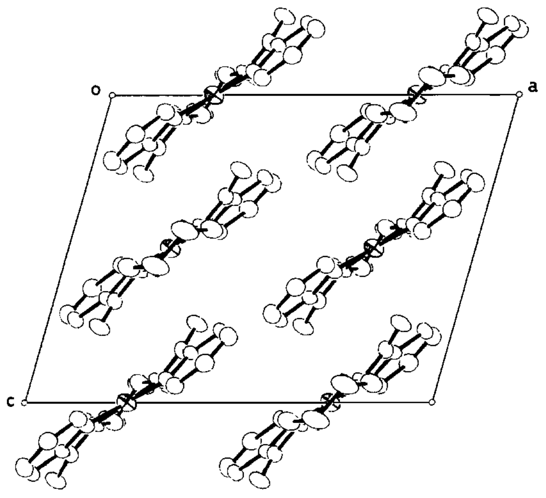

Fig. 2. Molecular packing in the cell viewed down *b*.

irregular square-plane (Table V, plane 1) which has a small tetrahedral twist of 5.7° at the nickel atom (Table V, planes 2 and 3). The Ni–N(*amide*) distance of 1.868(7) Å agrees well with Ni–N(*peptide*) and Ni–N(*amide*) distances in other square-planar nickel(II) complexes [7]. The Ni–N(*pyridine*) distance of 1.944(8) Å is as expected longer than the Ni–N(*amide*) distance.

As has been described [8] for similar N_4-tetra dentates truely planar coordination creates significant steric strain within the ligand. The pyridine ring is planar (Table V, plane 4), whilst the amide five-membered chelate ring deviates significantly from planarity (Table V, plane 5), the nickel atom being displaced by 0.08 and 0.42 Å from each plane respectively. The non-planarity in the picolinamide moiety can be described as the composite of two bond rotations; an anticlockwise twist about N(1)–C(O) of 22.2° and a clockwise twist about C(O)–C(11) of 12.0°. The combination of these rotations and the tetrahedral twist results in the observed dihedral angle of 24.5° between the planes of the pyridine ring and its symmetry related ring. Such an orientation alleviates the steric interaction between the pyridyl hydrogens in the 6-positions (H(15)···· H(15′) = 2.17 Å).

The carbonyl carbon atom has the expected trigonal-planar geometry (Table V, planes 10–12), but the amide nitrogen deviates considerably from trigonal-planarity towards a pyramidal arrangement. The distortion, as defined by the dihedral angles between the relevant three atom planes (Table V, planes 13–16), is intermediate between a trigonal-planar and pyramidal geometries, with the average angle being 30.8°; this nitrogen geometry would therefore be better described as a flattened pyramid rather than a distorted trigonal plane. This angle is much larger than that of 10.0 and 14.5° found in $[Cu(\textit{trans}\text{-bpch})H_2O]H_2O$ [2] and of 20.7 and 22.5° in $[Cu(\textit{cis}\text{-bpch})H_2O$ [3]. This large distortion at the amide nitrogen together with non-planarity of the picolinamide group reflects the inability of square-planar nickel to accommodate an out-of-plane distortion which was observed in the structures of copper(II) analogues [2, 3].

The cyclohexane ring adopts a slightly skewed chair conformation with the two methine hydrogens in a *trans* configuration. The three-atom plane (Table V, plane 7) makes a dihedral angle of 54.2° with the 'seat' of the chair (Table V, plane 6).

That the *cis*-isomer of the ligand does not yield a crystalline complex with nickel can be explained by its lack of ability to accommodate the out-of-plane distortion necessary to eleviate the steric interactions described for the analogous copper complex [3].

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