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Studies on the Metal–Amide Bond. XIX*. A Comparison of Molecular Distortions in the Crystal Structures of [*N,N*′-Bis(2′-pyridinecarboxamido)-1,2-benzene]nickel(II) with its 6′-Methyl-substituted Analogue

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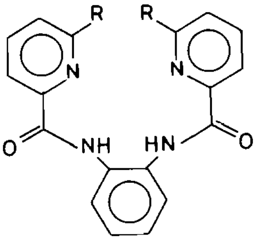
Abstract

[*N,N*′-Bis(pyridine-2′-carboxamide)-1,2-benzene]-nickel(II) monohydrate, $C_{18}H_{14}N_4O_3Ni$, crystallizes in the monoclinic space group *C2/c* with $a = 14.240(4)$, $b = 20.071(3)$, $c = 16.275(2)$ Å, $\beta = 97.25(2)^\circ$, $Z = 12$ and its crystal structure has been refined to $R = 0.033$ for 3597 diffractometer data. [*N,N*′-Bis(6′-methylpyridine-2′-carboxamide)-1,2-benzene]nickel(II) monohydrate, $C_{20}H_{18}N_4O_3Ni$, crystallizes in the orthorhombic space group *Pbca* with $a = 10.14(2)$. $b = 17.12(2)$, $c = 21.11(5)$ Å, $Z = 8$ and its crystal structure has been refined to $R = 0.088$ for 1979 photographic data. In both structures the nickel atoms are four coordinate with the ligands acting as N_4 tetradentates. For the first mentioned complex the structure consists of two independent molecules one of which is constrained, by space group requirements, to have C_2 (2) symmetry. These two molecules are closely similar and both exhibit nearly planar molecular arrangements with a small tetrahedral twist of up to 4° at the nickel atoms. In the second complex the methyl substitution at the 6′-pyridyl positions causes severe steric strain in the molecule which gives rise to a 14.9° tetrahedral twist at the nickel atom and approximately 25% pyramidal distortion at both amide nitrogen atoms. The resulting methyl–methyl separation of 3.26(1) Å is considerably less than the sum of the van der Waals radii for two such groups. This close separation leads to carbon-acid character for the methyl group protons which are shown to exchange for deuterons in NMR studies. A full analysis of the out-of-plane distortions and torsion angles of the two structures and a comparison with the previously reported analogous copper structures are made.

Introduction

The steric effects enforced by the planar N_4 coordination of the bis-picolinamide ligands described thus far in this series of papers have highlighted the close intramolecular contact involving the hydrogen atoms in the pyridyl 6′-positions. The enhanced steric interaction induced by methyl substitution in these positions has been demonstrated for the related ligands $bpbH_2$ (**I**) and 6-Me$bpbH_2$ (**II**) in the crytal structures of the deprotonated Cu(II) complexes [1, 2]. An analysis of the out-of-plane distortions and torsion angles in these structures [2] indicate that the steric strain is relatively uniform throughout the substituted ligand with no particular site being regarded as a major distortion centre. However the stereochemistry of the copper atom changes from square-based pyramidal to tetragonally distorted octahedral for the substituted ligand.

We now report the structures of the related nickel(II) complexes namely, Ni(bpb) and Ni(6-Mebpb). Both complexes are diamagnetic, indicating that the metal atom stereochemistries are essentially similar and square-planar. This adds a further constraint which was not applicable to the copper complexes.



I, R = H
II, R = Me

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*Part XVIII, is ref. 13.

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TABLE I. Summary of the Crystal Data, Data Collection and Refinement for the Complexes

<table>
<tr><td>Formula</td><td>Ni(bpb)·H_2O
$C_{18}H_{14}N_4O_3Ni$</td><td>Ni(6-Mebpb)·H_2O
$C_{20}H_{18}N_4O_3Ni$</td></tr>
<tr><td>M_r</td><td>393.05</td><td>421.1</td></tr>
<tr><td>Crystal</td><td></td><td></td></tr>
<tr><td>Colour</td><td>red</td><td>red–orange</td></tr>
<tr><td>Habit</td><td>0.64 × 0.36 × 0.34 mm</td><td>(100) elongated plates</td></tr>
<tr><td>Recrystallisation</td><td>nitrobenzene</td><td>chloroform</td></tr>
<tr><td>System</td><td>monoclinic</td><td>orthorhombic</td></tr>
<tr><td>a (Å)</td><td>14.240(4)</td><td>10.14(2)</td></tr>
<tr><td>b (Å)</td><td>20.071(3)</td><td>17.12(2)</td></tr>
<tr><td>c (Å)</td><td>16.275(2)</td><td>21.11(5)</td></tr>
<tr><td>β (°)</td><td>97.25(2)</td><td>–</td></tr>
<tr><td>U(Å^3)</td><td>4614.7</td><td>3664.6</td></tr>
<tr><td>D_m (flotation)</td><td>1.67</td><td>1.51</td></tr>
<tr><td>Z</td><td>12</td><td>8</td></tr>
<tr><td>D_c (g cm^{-3})</td><td>1.697</td><td>1.526</td></tr>
<tr><td>F(000)</td><td>2048</td><td>1744</td></tr>
<tr><td>μ (cm^{-1})</td><td>12.9 (Mo Kα)</td><td>13.7 (Cu Kα)</td></tr>
<tr><td>Space group</td><td>$C2/c$ (No. 15)</td><td>$Pbca$ (No. 61)</td></tr>
<tr><td>Intensity data</td><td></td><td></td></tr>
<tr><td>Collection method</td><td>Nicolet XRD P3 four-circle diffractometer [6] (Mo Kα), $\theta/2\theta$ scan technique, maximum Bragg angle θ = 26°</td><td>Equi-inclination Weissenberg photographs (Cu Kα), estimated visually from layers $h0-3l$, $0-4kl$, $hk0-2$</td></tr>
<tr><td>Temperature (°C)</td><td>−140</td><td>room temperature</td></tr>
<tr><td>Absorption corrected</td><td>yes transmission factors 0.868–0.906</td><td>no</td></tr>
<tr><td>Total reflexions</td><td>4241</td><td>2530</td></tr>
<tr><td>Reflexions for analysis</td><td>3597[a] ($I > 3\sigma I$)</td><td>1979</td></tr>
<tr><td>Refinement</td><td></td><td></td></tr>
<tr><td>Least-squares</td><td colspan="2">full-matrix</td></tr>
<tr><td>Weighting</td><td>counter statistics</td><td>$(3.0 + 0.015|F_o| + 0.0015|F_o|^2)^{-1}$</td></tr>
<tr><td>Anisotropic</td><td colspan="2">all non-H atoms</td></tr>
<tr><td>Hydrogen atoms</td><td colspan="2">included but not refined</td></tr>
<tr><td>Final (Δ/σ) maximum</td><td colspan="2">0.1</td></tr>
<tr><td>R</td><td>0.033</td><td>0.088</td></tr>
<tr><td>R'</td><td>0.034</td><td>0.119</td></tr>
<tr><td>Δ map, ρ(e Å^{-3})</td><td><0.5</td><td><0.6</td></tr>
<tr><td>Computer</td><td>FACOM M340S</td><td>UNIVAC 1106</td></tr>
<tr><td>Programs</td><td colspan="2">written by F.S.S.</td></tr>
</table>

[a] Reflexions 020 and 111 are included in the final R-value but were omitted from the refinement as they are much underestimated (extinction effects).

Experimental

The complexes were prepared as previously outlined [3, 4]. Crystal data, data collection and refinement details are summarised in Table I. Neutral-atom scattering factors were taken from International Tables for X-ray Crystallography [5] and the structures were solved by the heavy-atom method. For Ni(bpb) with $Z = 12$ the solution of the structure requires two independent molecules in the asymmetric unit one of which is constrained to possess $C_2(2)$ symmetry. Final atomic coordinates for the non-hydrogen atoms are given in Tables II and III.

Discussion

Perspective drawings [7] of the individual coordination molecules together with their atom labelling schemes are shown in Fig. 1. The packing of the molecules in the lattices including the hydrogen-bond networks are depicted in Fig. 2 and close intermolecular contacts are listed in Table IV. The molecular symmetry of the complex molecules is $C_2(2)$ with that for molecule 2 of Ni(bpb) being imposed by space group requirements. In the Ni(bpb) crystals the two independent molecules lie closely parallel to the (302) plane with a separation of ~3.2 Å; a unit of three molecules is so form-

TABLE II. Final Atomic Coordinates (fractional × 10^4) for Non-hydrogen Atoms with Estimated Standard Deviations in Parentheses for Ni(bpb)

	x	*y*	*z*
Ni(1)	3063.3(2)	2740.3(2)	1202.6(2)
N(111)	3220(2)	3691(1)	1008(1)
N(11)	3747(2)	2646(1)	321(1)
N(12)	3088(2)	1818(1)	1224(1)
N(121)	2272(2)	2637(1)	2085(1)
C(111)	3683(2)	3804(1)	343(2)
C(112)	3860(2)	4431(1)	59(2)
C(113)	3551(2)	4987(1)	466(2)
C(114)	3100(2)	4878(1)	1152(2)
C(115)	2952(2)	4231(1)	1411(2)
C(101)	4001(2)	3194(1)	−74(2)
O(11)	4434(1)	3232(1)	−683(1)
C(11)	3916(2)	1983(1)	83(2)
C(12)	3554(2)	1513(1)	608(2)
C(13)	3670(2)	835(1)	473(2)
C(14)	4126(2)	630(1)	−189(2)
C(15)	4474(2)	1094(1)	−716(2)
C(16)	4367(2)	1773(1)	−576(2)
O(12)	2601(1)	890(1)	1927(1)
C(102)	2648(2)	1498(1)	1786(2)
C(121)	2155(2)	1988(1)	2280(2)
C(122)	1600(2)	1781(1)	2864(2)
C(123)	1125(2)	2250(1)	3283(2)
C(124)	1235(2)	2914(1)	3085(2)
C(125)	1801(2)	3083(1)	2487(2)
Ni(2)	5000	2816.2(2)	2500
N(211)	4387(2)	2246(1)	3243(1)
N(21)	4493(2)	3501(1)	3070(1)
C(211)	3925(2)	2616(1)	3771(2)
C(212)	3468(2)	2330(1)	4379(2)
C(213)	3441(2)	1640(2)	4459(2)
C(214)	3890(2)	1267(1)	3915(2)
C(215)	4362(2)	1579(1)	3330(2)
C(201)	3944(2)	3351(1)	3646(2)
O(21)	3473(1)	3728(1)	4044(1)
C(21)	4714(2)	4150(1)	2822(2)
C(26)	4441(2)	4749(1)	3152(2)
C(25)	4728(2)	5352(1)	2826(2)
O(w1)	1914(2)	4550(1)	3172(1)
O(w2)	5000	132(2)	2500

ed in which molecule 2 is sandwiched between two of molecule 1 with the three nickel atoms almost co-linear and having an Ni(2)••Ni(1) separation of 3.259(1) Å. The orientation of the two independent molecules is such that they are rotated *ca.* 138° relative to each other about the Ni••Ni direction. The relative orientations of the three molecules in this trimeric unit are shown in Fig. 3. This arrangement is like that found in the π-sandwich compounds of the planar macrocyclic Ni(II) complexes derived from vic-dioximes [8] and is similarily suggestive of π-bonding between the molecules with little or no nickel–nickel interaction.

TABLE III. Final Atomic Coordinates (fractional × 10^4) for Non-hydrogen Atoms with Estimated Standard Deviations in Parentheses for Ni(6-Mebpb)

	x	*y*	*z*
Ni	674.8(14)	823.4(7)	1910.0(5)
N(11)	−226(7)	860(4)	1085(3)
N(1)	−492(7)	20(4)	2066(3)
N(2)	1028(7)	742(4)	2765(3)
N(21)	2203(7)	1517(4)	1914(3)
C(11)	−873(8)	164(4)	991(3)
C(12)	−1520(9)	−5(5)	428(4)
C(13)	−1583(10)	562(6)	−33(4)
C(14)	−1045(10)	1292(5)	91(4)
C(15)	−359(8)	1430(5)	658(3)
C(m15)	103(9)	2236(5)	800(4)
C(01)	−965(9)	−348(5)	1555(4)
O(1)	−1485(7)	−1015(3)	1533(3)
C(1)	−556(9)	−245(4)	2703(3)
C(2)	316(9)	178(4)	3093(3)
C(3)	418(10)	−11(5)	3733(4)
C(4)	−358(11)	−608(6)	3973(4)
C(5)	−1286(11)	−1006(5)	3589(4)
C(6)	−1352(11)	−821(5)	2937(4)
O(2)	1888(7)	1482(3)	3590(2)
C(02)	1737(9)	1334(4)	3010(4)
C(21)	2422(8)	1793(4)	2507(4)
C(22)	3296(10)	2362(5)	2642(4)
C(23)	4070(10)	2680(5)	2165(5)
C(24)	3946(9)	2347(5)	1560(4)
C(25)	3038(9)	1757(5)	1443(4)
C(m25)	2958(10)	1361(6)	809(4)
O(w)	1792(7)	2815(4)	4387(3)

Table V gives selected molecular dimensions. The respective bonding parameters of the two independent Ni(bpb) molecules are very similar. Both exhibit an almost planar molecular arrangement similar to that observed in the related Ni(bpen) structure [9]. This is in contrast with the analogous copper(II) structures [1, 10] in which the preferred square-based pyramidal coordination gives rise to distortions in the amide groups. A full analysis of distortions from planarity, together with the torsion angles in the 'peptide units', for the present structures and Ni(bpen) is given in Table VI. The near molecular planarity of the Ni(bpen) and Ni(bpb) structures is apparent from the small distortions in the 'peptide units' and at the nickel atoms. The accumulative effect of the small twists around individual bonds in the ligands for these structures alleviates steric strain associated with the close intramolecular contacts of the 6'-pyridyl hydrogen atoms. The structure analysis of Ni(6-Mebpb) clearly shows that methyl substitution in the 6'-pyridyl position results in severe distortion of the molecule relative to the unsubstituted structure.

TABLE IV. Contact Distances (Å) with Estimated Standard Deviations in Parentheses

Ni(bpb)		Ni(6-Mebpb)	
(a) Proposed donor–acceptor hydrogen-bond distances[a]			
O(W1)–H(W12)···O(12$^{\text{i}}$)	2.787(3)	O(W)–H(W2)···O(1$^{\text{iii}}$)	2.806(8)
O(W1)–H(W11)···O(21)	2.978(3)	O(W)–H(W1)···O(2)	2.837(8)
O(W2)–H(W2)···O(W1$^{\text{ii}}$)	3.040(2)		
(b) Intermolecular distances <3.3 Å[a]			
C(115)···C(21)	3.184(4)	N(11)···O(2$^{\text{vii}}$)	3.188(8)
C(12)···C(215$^{\text{iv}}$)	3.243(4)	C(15)···O(2$^{\text{vii}}$)	3.213(9)
O(11)···C(121$^{\text{v}}$)	3.253(3)		
O(11)···C(123$^{\text{vi}}$)	3.254(3)		
Ni(1)···Ni(2)	3.259(1)		

[a] Roman numeral superscripts refer to the following equivalent positions relative to x, y, z; (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$, (ii) $\frac{1}{2} + x, y - 1, z$; (iii) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $1 - x, y, \frac{1}{2} - z$; (v) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (vi) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$; (vii) $x - \frac{1}{2}, y, \frac{1}{2} - z$.

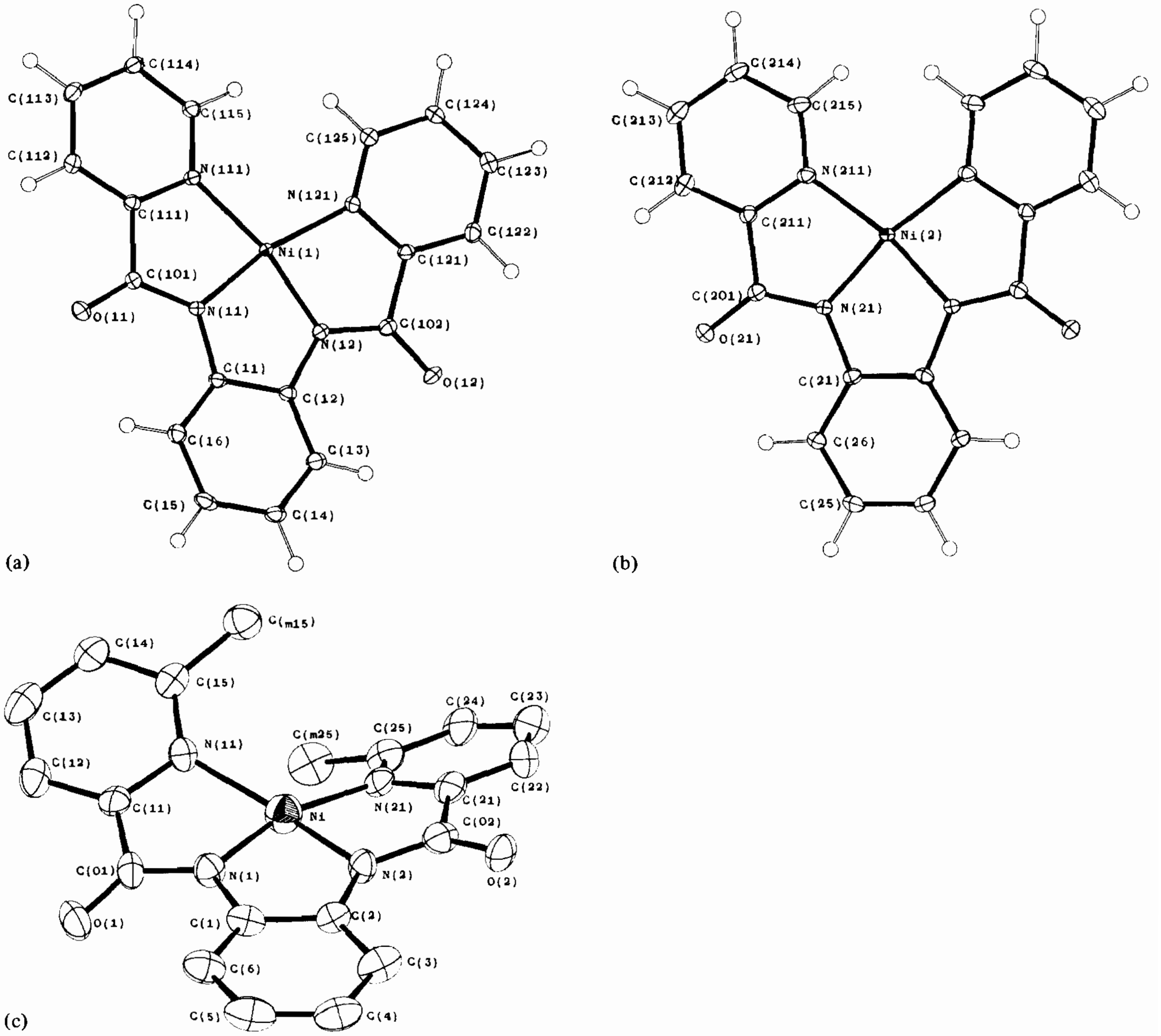

Fig. 1. Perspective drawings of the chelated molecules with the atom labelling schemes. Thermal ellipsoids are drawn to include 35% probability. (a) Ni(bpb) molecule **1**, (b) Ni(bpb) molecule **2** and (c) Ni(6-Mebpb).

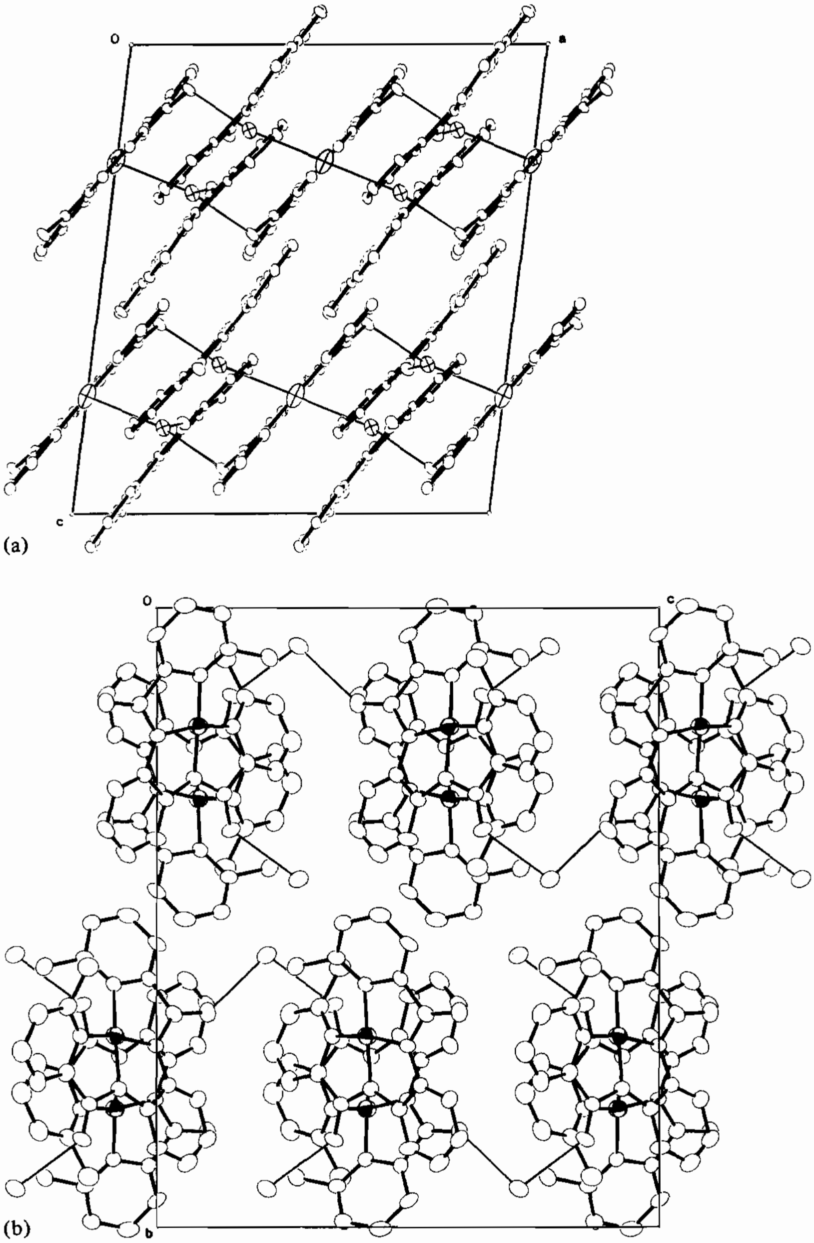

Fig. 2. The packing of the molecules in the unit cells with the hydrogen bonds represented by thin lines. (a) Ni(bpb) and (b) Ni(6-Mebpb).

For Ni(6-Mebpb) the planarity of the molecule as a whole is destroyed with the main distortions being a 14.9° tetrahedral twist at the nickel atom and approximately 25% pyramidal distortion at both amide nitrogen atoms. The pyridyl methyl carbon atoms are 3.26(1) Å apart which is 0.1 Å less than that observed in the analogous copper structure [2] and some 0.75 Å less than the sum of the van der Waals radii for two methyl groups [11]. Even though the folding in the pyridyl rings to give a 'boat' distortion is similar to that in the copper structure [2] the pyramidal distortions at their nitrogen and C(*n*5) carbon atoms is less marked. Once again the severe 'B-strain' effect [12] resulting from the planar coordination of the tetradentate ligand is observed.

Relief of the steric strain which, like Cu(6-Mebpb), is manifest in the structure of Ni(6-Mebpb) is not restricted to any atom or bond in particular. However, there seems to be more distortion in one of the picolinamide groups as indicated by the larger pyramidal distortions at the N(11) and C(15) atoms and

TABLE V. Selected Molecular Dimensions with Estimated Standard Deviations in Parentheses

	Ni(bpb)		Ni(6-Mebpb)
	molecule 1	molecule 2	
(a) Distances (Å)			
Ni–N(py)	1.948(2)	1.949(2)	1.960(7)
Ni–N(am)	1.847(2)	1.854(2)	1.844(7)
C(py)–C(am)	1.498(3)	1.490(4)	1.486(11)
C(am)–O(am)	1.240(3)	1.247(3)	1.259(10)
C(am)–N(am)	1 341(3)	1.329(3)	1.342(10)
N(am)–C	1.412(3)	1.411(3)	1.406(10)
(b) Angles (°)			
N(py)–Ni–N(py)	108.3(1)	108.1(2)	110.7(3)
N(am)–Ni–N(am)	84.3(1)	84.3(1)	83.9(3)
N(py)–Ni–N(am)	83.7(1)	83.8(1)	83.4(3)
C(py)–C(am)–O(am)	120.9(2)	120.7(2)	122.1(8)
C(py)–C(am)–N(am)	109.9(2)	110.1(2)	111.0(7)
N(am)–C(am)–O(am)	129.2(2)	129 2(2)	126.7(8)
Ni–N(am)–C(am)	119.0(2)	119.0(2)	115.5(5)
Ni–N(am)–C	115.6(2)	115.2(2)	115.9(5)
C(am)–N(am)–C	125.2(2)	125.7(2)	127.1(7)

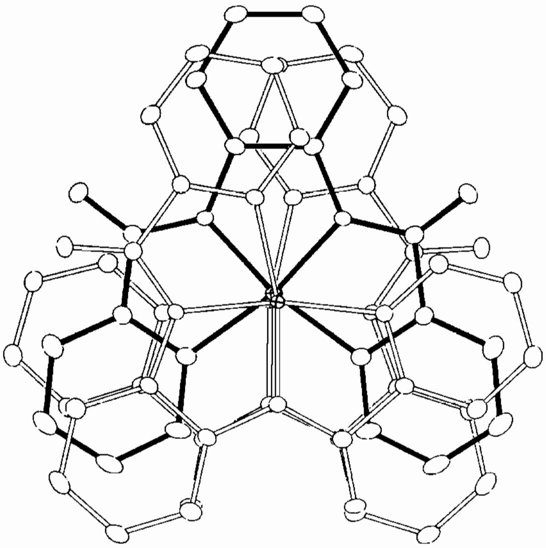

Fig. 3. The relative orientations of the three Ni(6-Mebpb) molecules in the trimeric unit projected perpendicular to the stacking plane.

TABLE VI. Data for the Analysis of Distortions in the Complex Molecules with Angles (°) and Distances (Å). Detailed Definitions of Distortions and Torsion Angles are given in Fig. 3 and Table VI of ref. 2.

	Ni(bpen)	Ni(bpb)		Ni(6-Mebpb)
		molecule 1	molecule 2	
Reference	8		this work	this work
Ni atom tetrahedral twist[a]	1.5	4.1	2.2	14.9
Pyramidal distortions				
C(On)	1.2	0.4, 0.6	1.3	3.4, 3.5
N(n)	2.6	3.7, 2.5	2.0	14.3, 13.9
N(n1)	0.2	0.1, 3.6	1.5	4.3, 0.3
C(n5)	–	–	–	5.8, 1.1
Pyridyl ring distortions				
γ	0.5	3.0, 0.9	1.2	9.8, 10.6
δ	0.3	1.8, 0.6	0.6	5.6, 6.4
Torsion angles and specific distortions about the 'peptide unit'				
$\Delta\psi_{CC}$	−1.2	−0.2, −4.1	−5.2	12.9, 7.0
$\Delta\omega$	∧3.9	−1.4, ∧5.7	3.4	−7.9, −3.1
θ_N	−2.6	3.8, 2.6	2.1	−14.9, −13.9
θ_C	∧1.2	0.4, ∧0.6	−1.3	−3.3, −3.4
$\Delta\phi_{NC}$	6.7	1.0, −2.6	2.1	−14.9, −13.9
Pyridyl–pyridyl contacts				
C(15)···C(25)	3.45(2)	3.433(4)	3.410(6)	–
H(15)···H(25)	1.81	1.82	1.81	–
C(m15)···C(m25)	–	–	–	3.26(1)

[a] Taken as the average dihedral angle between N_3 planes.

the greater magnitudes for $\Delta\psi_{CC}$ and $\Delta\omega$. The closer 6–6′ methyl separation in the present structure probably reflects a compromise between the repulsive effects of these groups and the extent to which the nickel atom can distort from square-planar coordination. In the copper structure [2] the stereochemistry of the copper changes to a distorted octahedron which includes a larger tetrahedral twist of 16.7° at the Cu atom, hence the greater methyl–methyl separation.

A proton NMR study of Ni(6-Mebpb) demonstrates an interesting effect caused by the strain associated with the compound's enforced methyl–methyl interaction. The spectrum of the complex dissolved in CD_3OD–D_2O (1:1) shows a sharp singlet resonance at 2.38 ppm attributable to the CH_3 groups. Over a period of several days this signal disappears completely, and associated with this is a small downfield shift of the H(*n*4) resonances at ~7.75 ppm. On addition of NaOD to a fresh solution of the complex this process begins immediately and is complete after a few hours. This facile exchange of the methyl group protons for solvent deuterons demonstrates their significant carbon-acid character, which in turn must be induced by the observed steric crowding.

Supplementary Material

Lists of observed and calculated structure factors and Tables of anisotropic thermal parameters, of hydrogen atom parameters, of complete intramolecular dimensions and of least-squares planes and their equations have been deposited with the Editor-in-Chief.

Acknowledgement

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