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Preparation and Crystal Structure of Bis-(benzoylbenzamidine)nickel(II)

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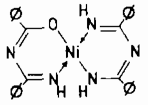
The crystal structure of a reaction product of Raney Nickel and benzonitrile, the diamagnetic complex bis-*(benzoylbenzamidine)nickel(II), has been determined and refined to* R *0.068 for 1372 reflections measured on a single-crystal diffractometer with MoKα radiation. The unit-cell of* $Ni[OC(C_6H_5)NC(C_6H_5)NH]_2$ *has dimensions* a = *25.455(20),* b = *5.692(5),* c = *18.371(13) Å, β = 117.45° (5), belongs to space-group C2/*c, *and contains four molecules. The nickel atoms are required to be at symmetry centres and the bidentate ligands around the nickel atom are in a* trans *square-planar arrangement; the Ni–N and Ni–O distances are 1.832(8) and 1.837(4) Å, resp. with an intrachelate N–Ni–O angle of 91.4°. The molecular skeleton is almost planar with torsion angles of about 5° around the exocyclic C–C bonds. The pattern of bond distances of the ligands is indicative of considerable electron-delocalisation in the molecule. Strain is limited to repulsion of aromatic hydrogen atoms and lone electron pairs in the* ortho *positions of the adjacent chelate rings. The ligands are also affected by angular distortions due to coordination. The assignment of the molecular structure is in agreement with other physico-chemical data.*

Introduction

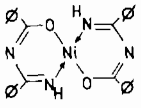
In the last few years various studies have appeared on the activation of the C≡N triple bond by π-complex formation with transition metals via cycloaddition, in analogy to reactions involving the acetylenic bond. However, in the former case π-complexation is more difficult due to the ready formation of σ-complexes involving the free-electron pair residing at the nitrogen atom.

In view of previous investigations on this subject in this Institute [1–6], we have become interested in Heldt's paper [7] reporting the formation of triphenyltriazine from benzonitrile and Raney Nickel in dry N_2 atmosphere by cyclomerization involving a π-complex of benzonitrile and Ni(0). Following Heldt's experimental procedure, after various attempts we have succeeded in obtaining modest quantities of a stable product which in recrystallized form consists of tiny yellow–orange acicular crystals. As mass spectroscopy indicates a parent ion peak at m/e = 503, corresponding to $C_{28}H_{23}N_5ONi$, the following planar chelate structure is proposed for this diamagnetic product:



I

A similar investigation has also been made by Oehme and Pracejus [8] who independently come to the conclusion that a reaction product is being formed which is different from that advanced by Heldt. They also noticed that this compound is more readily obtained in the presence of Ni^{2+} and H_2O and in atmospheric conditions. The compound, $C_{28}H_{24}N_4O_2Ni$, was claimed to be the chelate of Ni(II) with two molecules of benzoylbenzamidine, identical with *bis*-(iminodibenzamid)nickel(II), $C_{28}H_{22}N_4O_2Ni$, which had been described as early as 1913 by Ley and Werner [9], namely:



II

In view of the conflicting nature of previous work, we have now reprepared the complex according to the procedure of ref. [8], *i.e.* from benzonitrile and Raney Nickel in air. As *bis*-(benzoylbenzamidine)-nickel(II) differs from chelate (I) by the substitution of an imino-grouping for an oxygen atom, its molecular ionic mass differs by one unit (m/e = 504).

As the proposed chelate structures of Ni(II) obviously exclude the participation of Ni(0) to the cyclotrimerization reaction, we have carried out an X-ray crystal structure determination of product (II) to confirm its molecular structure.

Experimental

Preparation of Compounds

*(Benzoylbenzamidine)(*bis*-benzamidine)nickel(II), Ni[OC(C_6H_5)NC(C_6H_5)NH] · [HNC(C_6H_5)NC(C_6H_5)NH], (I)*

P_2O_5-dried benzonitrile (85 ml) was added to Raney Nickel (25 g) which had been washed with dry acetone and degassed at 0.1 mmHg pressure; the mixture was heated to reflux with stirring for 48 h. After cooling, and filtration of Raney Nickel excess benzonitrile was distilled off. The dry residue was repeatedly washed with petroleum ether and hot water. The residue was subsequently extracted with methanol. After removing the solvent the product (about 0.5 g) was recrystallized repeatedly from toluene and CCl_4. The yellow–orange acicular crystals decompose without melting at 251–4 °C (Koffler hot-stage). *Anal. Found:* C, 64.8; H, 4.4; N, 13.5%; Ni, not detd. *Calcd.* for $C_{28}H_{23}N_5ONi$: C, 66.7; H, 4.6; N, 13.8; Ni, 11.7%. The analytical data are strongly influenced by traces of metallic Ni. However, the ratio C/N (calcd. 5.60, obsd. 5.59) as well as the ratio N/O (calcd. 5.0, obsd. 4.8), the latter obtained from the products of pyrolysis (benzonitrile, NH_3 and N_2 for N; H_2O for O), appear to confirm the proposed stoichiometry.

Bis-*(benzoylbenzamidine)nickel(II), Ni[OC(C_6H_5)NC(C_6H_5)NH]$_2$, (II)*

Raney Nickel (15 g), washed with ethanol and benzonitrile, was added to benzonitrile (100 ml). The mixture was heated and the fraction boiling at 130 °C was removed by distillation. The resulting mixture was refluxed in dry air (P_2O_5) for 16 h with stirring. After filtration followed by cooling the complex crystallized. Subsequent washing with hot water and recrystallization in toluene gave yellow–orange acicular crystals. *Anal.: Found:* C, 67.0; H, 4.4; N, 11.1; Ni, 11.4%. *Calcd.* for $C_{28}H_{22}N_4O_2Ni$: C, 66.6; H, 4.3; N, 11.1; Ni, 11.6%.

X-Ray Analysis

Crystals of *bis*-(benzoylbenzamidine)nickel(II) (hereafter called Ni(beam)$_2$), obtained from solutions of CCl_4, benzene or toluene are acicular and unsuitable for data collection; mixtures of acetone and methanol lead again to acicular crystals which however contain MeOH as a solvate. Crystals suitable for the diffraction experiments were finally obtained from mixtures of EtOH, C_6H_6 and acetone in the form of parallelopipeds.

Yellow–orange crystals of (II) were firmly mounted in Lindemann glass capillary tubes. Preliminary space-group and unit-cell dimensions were obtained from Weissenberg photographs.

A crystal of parallelopipedal shape (0.4 × 0.35 × 0.5 mm) was mounted on a Picker FACS1 four-circle computer-controlled X-ray diffractometer equipped with a scintillation counter and a pulse-height discriminator. The orientation matrix and refined unit-cell dimensions were obtained from a least-squares fit of χ, ϕ, ω and 2θ values from 12 independent reflections of medium intensity.

Crystal Data

$C_{28}H_{22}N_4O_2Ni$: Mol. wt. 505.23; monoclinic, a = 25.455(20), b = 5.692(5), c = 18.371(13) Å, β = 117.45(5)°; U = 2362.09 Å^3; D_c = 1.42 g cm^{-3}; Z = 4; F(000) = 1048. Space-group $C2/c$, from systematic absences (hkl) for $h + k$ odd, ($h0l$) for l odd, and from structure determination. MoKα radiation, λ = 0.71069 Å, μ(MoKα) = 8.77 cm^{-1}.

Intensities of X-ray reflections within two octants of the reciprocal sphere were collected by use of Zr-filtered MoKα radiation up to $2\theta \leqslant 50°$. The moving-crystal–moving-counter technique was used with a 2θ scan speed of 1° min^{-1} and a scan range of 2.0–2.5° in order to allow for the greater separation of the Kα_1 and Kα_2 peaks at increasing 2θ values. Stationary background measurements were made during 10 sec at each end of every 2θ scan. Three standard reflections were monitored periodically to detect systematic changes during the course of the data collection. The scale factor determined by these standard reflections was essentially constant, with only a random variation of ± 1% due primarily to counting statistics. Crystals of Ni(beam)$_2$ showed to be perfectly stable in the X-ray beam at least over the period of data collection. 2077 independent reflections were measured of which 1372 had $I \geqslant 3\sigma$. An arbitrary intensity equal to 0.5 times the observable limit was assigned to the 705 non-significant reflections. All intensities were corrected as usual for Lorentz and polarization effects. However, no corrections for absorption have been made in view of the low value of μ (8.77 cm^{-1}). A preliminary overall scale factor and overall temperature factor were estimated from the statistics of the normalized structure factors. The Wilson plot gave indications for a hypersymmetric intensity distribution.

Structure Determination and Refinement

The space-group $C2/c$ requires the nickel atoms to occupy a set of fourfold special positions ($4a$–$4e$), either with C_2 or C_i point symmetry [10]. However, on the basis of the expected geometry of the molecules of Ni(beam)$_2$ only the positions $4a,b$ or $4c,d$ can reasonably be proposed for the heavy atom. The former assumption was readily verified by the strong vector interactions of the three-dimensional Patterson function, calculated with Immirzi's FFSYNT program [11]. Consequently, and without loss of generality, Ni was located at (0, 1/2, 0). As a result, in the 3D-Fourier map, phased on these nickel positions, a mirror plane shows up at (x, 0, z) and (x, 1/2, z).

This mirror image was subsequently destroyed by the introduction of the phases of a few correctly placed atoms. Coordinates of the atoms of the whole molecule were found by successive $F(hkl)$ and $\rho(xyz)$ calculations.

Block-diagonal least-squares (BDLS) refinement was then performed with a program described by Immirzi [12]. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. Atomic scattering factors were calculated from the expression in ref. 13, using values for the parameters given by Moore [14]. The Cruickshank weighting scheme $1/w = A + B|F_o| + C|F_o|^2$ was adopted for the observed reflections, with $A = 2F_{\min}$, $B = 1.00$ and $C = 2/F_{\max}$ [15]. Unobserved reflections were treated with w = constant. After four cycles of BDLS refinement with isotropic temperature factors ($R = \Sigma|kF_o| - |F_c||/\Sigma k|F_o| = 0.11$) and four more cycles with anisotropic thermal parameters and overall scale factor ($R = 0.071$) aromatic hydrogen atoms were introduced in calculated positions (C–H, 1.08 Å; C–C–H, 120°) with isotropic thermal parameters ($B = 5$ Å^2) and were kept fixed. After introduction of these atoms refinement converged to $R = 0.068$, when the final shifts were well below the corresponding standard deviations. For the final cycle of the non-hydrogen atom refinement, the average shift/error for positional and thermal parameters was 0.2, with a maximum of 0.7. At this stage, a three-dimensional ΔF synthesis was phased on the heavy atoms, which revealed the presence of an imino hydrogen together with well-resolved maxima corresponding to the aromatic hydrogens. A structure factor calculation, including all hydrogen atoms in calculated positions and H and H(8) as observed, did not change R from its final value of 0.068. In the course of the refinement no extinction correction was applied to the data, as the strong reflections appeared to be unaffected.

An attempt to refine the structure in the non-centrosymmetric space-group *Cc* did not lead to any substantial improvement in the reliability factor nor to substantial deviations from a centrosymmetric structure.

All calculations were carried out on the UNIVAC 1110/20 computer of this Institute. The drawings were prepared with the aid of the ORTEP plotting programme (C. K. Johnson, Oak Ridge Natl. Labs.).

Results

The final positional and thermal parameters of the atoms, together with standard deviations estimated from the block-diagonal approximation in the usual way, are listed in Tables I and II. It is not likely that the calculated hydrogen coordinates in Table I are greatly different from the true values since no ambiguity is involved in determining the hydrogen configuration. The labelling of the atoms is shown in Fig. 1. The bond lengths and valence angles in the molecule, calculated from the coordinates of Table I, are shown in Table III. The thermal parameters of the chelate ring atoms are nearly isotropic and significantly less in magnitude than those of the phenyl groups. In the latter the motion of the atoms is markedly anisotropic; the smallest thermal movement is connected with the atoms directly bonded to the central ring and reasonably enough gradually increasing values are found for the most remote atoms (*cf.* Fig. 1).

TABLE I. Final Fractional Coordinates with Estimated Standard Deviations in Parentheses.[a]

Atom	x/a	y/b	z/c	B (Å^2)
Ni	0.5000(0)	1.0000(0)	0.5000(0)	
C(1)	0.5176(3)	0.6058(12)	0.4223(4)	
C(2)	0.4248(3)	0.7850(12)	0.3494(4)	
C(3)	0.3658(3)	0.7674(12)	0.2750(4)	
C(4)	0.3545(3)	0.5842(13)	0.2210(5)	
C(5)	0.2990(3)	0.5685(15)	0.1510(5)	
C(6)	0.2556(4)	0.7351(16)	0.1373(5)	
C(7)	0.2680(4)	0.9185(15)	0.1912(5)	
C(8)	0.3227(3)	0.9350(15)	0.2598(5)	
C(9)	0.5573(3)	0.4129(13)	0.4219(4)	
C(10)	0.6148(3)	0.3966(15)	0.4851(5)	
C(11)	0.6520(4)	0.2238(17)	0.4828(6)	
C(12)	0.6319(4)	0.0599(15)	0.4202(5)	
C(13)	0.5744(4)	0.0705(14)	0.3587(5)	
C(14)	0.5378(3)	0.2486(14)	0.3595(4)	
O	0.5363(2)	0.7387(9)	0.4850(3)	
N(1)	0.4641(2)	0.6173(10)	0.3560(3)	
N(2)	0.4342(2)	0.9515(10)	0.4016(3)	
H	0.407	1.069	0.391	5.0
H(4)	0.389	0.453	0.232	5.0
H(5)	0.290	0.423	0.108	5.0
H(6)	0.212	0.721	0.084	5.0
H(7)	0.234	1.052	0.179	5.0
H(8)	0.323	1.055	0.299	5.0
H(10)	0.630	0.522	0.536	5.0
H(11)	0.697	0.215	0.532	5.0
H(12)	0.662	−0.076	0.419	5.0
H(13)	0.558	−0.061	0.310	5.0
H(14)	0.492	0.259	0.310	5.0

[a] The coordinates of H and H(8) are those taken from the ΔF synthesis.

A list of structure factors has been deposited as Supplementary Publication No. SUP 90030 (2pp., 1 microfiche)*. Examination of the structure factors in terms of the magnitudes of $F_{\rm obs}$ showed poorest agreement between experimental and calculated values for the weakest reflections. Analysis of $\Sigma w\Delta^2/n$ to $|F_o|$ and $\sin^2\theta/\lambda^2$ showed the weighting scheme to be satisfactory.

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*Copies may be obtained from the British Library Lending Division, Wetherby (W. Yorkshire), U.K.

TABLE II. Anisotropic Thermal Parameters (Å^2) in the Form exp $-1/4$ $(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)$. Standard deviations are appended in brackets as units in the last place.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	2.99(4)	3.61(5)	2.75(4)	−0.16(5)	1.08(4)	−0.54(4)
C(1)	4.39(29)	3.41(27)	2.88(24)	−0.40(24)	2.17(22)	0.20(22)
C(2)	3.12(25)	3.95(31)	3.20(26)	−0.46(23)	1.47(22)	0.04(23)
C(3)	3.61(28)	4.01(31)	3.68(28)	−0.36(24)	1.68(24)	−0.02(25)
C(4)	3.17(27)	4.00(30)	4.72(33)	0.50(24)	1.16(25)	−1.26(27)
C(5)	4.25(34)	5.09(40)	5.03(36)	−0.12(29)	1.26(29)	−1.08(31)
C(6)	4.22(34)	5.87(44)	5.34(39)	−1.08(33)	1.57(31)	−0.57(36)
C(7)	4.40(35)	4.79(37)	5.49(39)	0.81(30)	1.16(30)	−0.04(33)
C(8)	4.25(32)	5.04(39)	4.50(33)	0.67(28)	1.60(27)	−1.14(29)
C(9)	4.40(31)	3.73(28)	3.21(26)	0.07(25)	2.18(24)	0.42(23)
C(10)	3.45(30)	4.73(35)	4.63(34)	−0.09(29)	0.61(26)	−0.43(30)
C(11)	3.93(34)	5.81(46)	6.43(46)	1.66(33)	0.97(33)	1.22(38)
C(12)	6.14(43)	4.76(42)	5.90(42)	1.58(33)	2.89(36)	1.35(33)
C(13)	5.74(38)	4.67(37)	4.20(33)	1.17(31)	2.47(30)	−0.09(28)
C(14)	4.34(31)	5.07(37)	3.38(28)	0.31(28)	1.73(25)	−0.76(27)
O	3.76(20)	4.42(23)	3.58(20)	0.01(18)	1.39(17)	−0.68(18)
N(1)	3.00(21)	3.79(25)	3.22(22)	−0.02(20)	0.62(18)	−0.51(20)
N(2)	3.12(21)	3.77(28)	3.30(21)	0.02(19)	0.91(17)	−0.94(19)

TABLE III. Molecular Parameters of Ni(beam)$_2$. Standard deviations are appended in brackets as units in the last place. (′) into atom labelling indicates the atoms related to those of the independent unit by the inversion centre.

Bond Lengths (in Å)		Bond Angles (in degrees)	
Ni–O	1.837(4)	O–Ni–N(2)	91.4(2)
Ni–N(2)	1.832(8)	O′–Ni–N(2)	88.6(2)
N(1)–C(1)	1.35(2)	Ni–O–C(1)	127.8(5)
N(1)–C(2)	1.35(1)	O–C(1)–N(1)	126.1(6)
N(2)–C(2)	1.29(1)	C(1)–N(1)–C(2)	121.1(6)
O–C(1)	1.27(1)	N(1)–C(2)–N(2)	125.2(4)
C(1)–C(9)	1.50(1)	C(2)–N(2)–Ni	128.1(7)
C(2)–C(3)	1.50(2)	N(2)–C(2)–C(3)	119.6(6)
C(3)–C(4)	1.38(1)	N(1)–C(2)–C(3)	115.2(5)
C(4)–C(5)	1.41(3)	C(2)–C(3)–C(8)	120.5(7)
C(5)–C(6)	1.39(2)	C(2)–C(3)–C(4)	119.8(6)
C(6)–C(7)	1.37(1)	N(1)–C(1)–C(9)	115.9(5)
C(7)–C(8)	1.39(3)	O–C(1)–C(9)	118.1(5)
C(8)–C(3)	1.38(2)	C(1)–C(9)–C(14)	121.1(5)
Average 1.38		C(1)–C(9)–C(10)	119.9(7)
C(9)–C(10)	1.39(3)	C(3)–C(4)–C(5)	119.7(7)
C(10)–C(11)	1.38(1)	C(4)–C(5)–C(6)	120.2(7)
C(11)–C(12)	1.38(2)	C(5)–C(6)–C(7)	119.3(6)
C(12)–C(13)	1.38(3)	C(6)–C(7)–C(8)	120.6(7)
C(13)–C(14)	1.38(1)	C(7)–C(8)–C(3)	120.5(7)
C(14)–C(9)	1.38(2)	C(8)–C(3)–C(4)	119.7(5)
Average 1.38		Average	120.0
N(2)–H	0.92	C(9)–C(10)–C(11)	119.7(7)
C(8)–H(8)	0.99	C(10)–C(11)–C(12)	120.6(6)
		C(11)–C(12)–C(13)	120.0(7)
		C(12)–C(13)–C(14)	119.4(6)
		C(13)–C(14)–C(9)	121.2(5)
		C(14)–C(9)–C(10)	119.0(6)
		Average	120.0

TABLE III. *(Continued)*

Bond Angles (in degrees)		Non-bonded distances (in Å)	
Ni–N(2)–H	111.1	H−−H(8)	2.02
C(2)–N(2)–H	120.7	H−−H(10′)	3.04
C(3)–C(8)–H(8)	126.2	H−−O′	2.33
C(7)–C(8)–H(8)	112.0	H(4)−−N(1)	2.39
		H(4)−−H(14)	2.60
		H(10)−−O	2.46

Torsion Angles (in degrees)	
C(4)–C(3)–C(2)–N(1)	2.16
C(4)–C(3)–C(2)–N(2)	182.87
C(8)–C(3)–C(2)–N(1)	182.64
C(8)–C(3)–C(2)–N(2)	3.35
C(14)–C(9)–C(1)–O	173.82
C(14)–C(9)–C(1)–N(1)	−4.39
C(10)–C(9)–C(1)–O	−6.04
C(10)–C(9)–C(1)–N(1)	175.75

Discussion

Molecular Structure

The structural results leave little doubt that the yellow–orange reaction product of Raney Nickel and benzonitrile is in fact a compound with structure (II) rather than a species involving a σ Ni–N bond and a dative Ni ←OH bond, which is a less likely possibility. Also, the single sharp infrared absorption at 3375 cm^{-1} in a Nujol mull (Fig. 2), which is assigned to the N–H stretching frequency, is consistent with the crystallographic data. Failure to observe any improvement upon refinement of the crystal structure in the non-centrosymmetric space-group *Cc* clearly excludes the occurrence of a *cis* structure for Ni(beam)$_2$.

The Nickel(II) Coordination Sphere

The symmetry of the ligand field around the nickel atom is D_{2h} $(2/m)$, *i.e.* higher than the overall symmetry of the complex (C_i, $\bar{1}$), as imposed by the space-group requirements. Bonding to nickel is therefore essentially square with the four σ-bonds formed by combining the ligand orbitals with the $d_{x^2-y^2}$, s, p_x and p_y orbitals of the metal, leaving a vacant p_z for π-bonding. It is noticed that, although the coordinate bonds are exactly coplanar and the Ni–O and Ni–N bond distances essentially equal, the configuration has a rhomboidal distortion (Ni–O 1.837 Å, Ni–N 1.832 Å, ∢ N–Ni–O 91.4°), which is probably on account of ligand–ligand repulsions (*cf.* N—N "bite" distance) or simply a residue of angle strain in the chelate rings.

For a correct evaluation of the Ni–N and Ni–O bond distances a critical comparison with other reported data on mono- and polynuclear nickel(II) complexes is in order. Nickel-donor atom distances show a rather broad range of values and vary greatly with the stereochemical configuration of the metal, the conformational demands of the ligands and with factors governing distortion of the nickel environment such as interligand repulsion, electronic distortion, spin state and crystal packing forces. We observe a gradual increase in Ni–N distances on passing from the ideal square-planar configuration to one involving stepping of the chelate rings in which the ligands are individually planar but not coplanar, *via* tetrahedrally deformed square-planar donor sets to the tetrahedral configuration. Five and six-coordinate nickel(II) exhibits even more stretched Ni–N and Ni–O bond lengths.

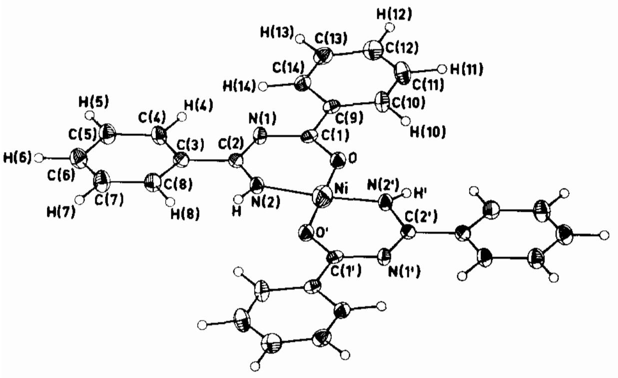

Fig. 1. View of the bis-(benzoylbenzamidine)nickel(II) molecule indicating the atom labelling scheme and the 30% probability thermal vibrations ellipsoids.

It is desirable then to compare the bond data of Ni(beam)$_2$ with those in unstrained configurations of oxygen and/or nitrogen atoms arranged in a square plane about a nickel atom. Ni–N bond distances in square-planar complexes involving trigonal nitrogen atoms have been observed in a wide range from 1.81–1.98 Å. It is evident that various factors influence this feature. Obviously, an important disturbing factor, intraligand strain, is absent in complexes with monodentate ligands. Only one crystal structure determination with four monodentate nitrogen atoms has been reported, namely tetrakis(3,4-dimethylpyridine)nickel(II) perchlorate [16]. Apart from disorder in this structure, the Ni–N(pyridine) distance (1.897 Å) is here probably strained as a similar distance of 1.939 Å in butane-2,3-dione-bis-(2'-pyridyl-hydrazonato)-nickel(II), [Ni(BDPH)–2H], is reported as stretched compared to the Ni–N(imine) distance of 1.828 Å [17]. Similarly, the Ni–N(pyridine) bond length of 1.92–3 Å in bis-(pyridine-2-carboxamido)nickel(II) dihydrate [18, 19] is also ascribed to steric hindrance offered by the pyridine ring. In discussing coordinate bonds further caution is required since the distances observed in otherwise similar systems with different ring constraints also vary over rather wide ranges. This is clearly demonstrated in the molecular structure of (4-methyliminopentane-2,3-dione-3-oximato)

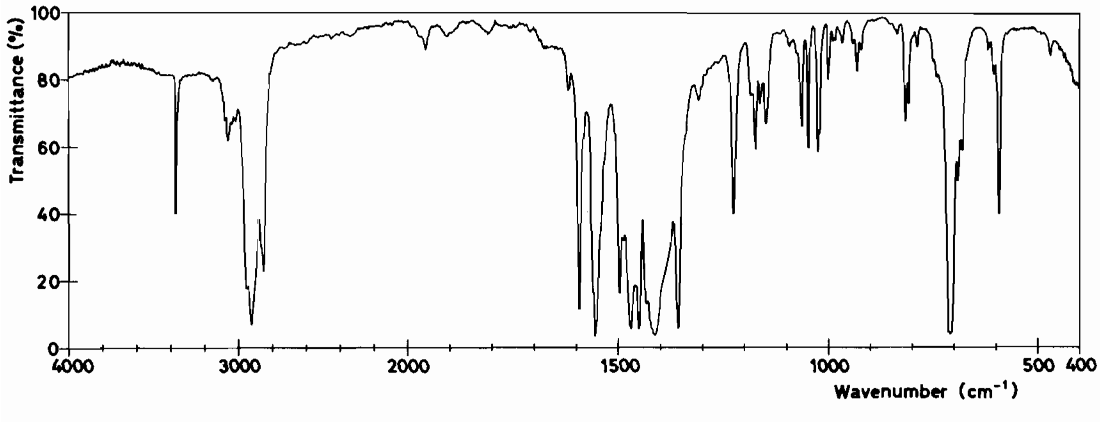

Fig. 2. Infrared spectrum (Nujol mull) of bis-(benzoylbenzamidine)nickel(II).

TABLE IV. Averaged Nickel(II)–Nitrogen and Nickel(II)–Oxygen Bond Data in Complexes with Square-Planar Donor Sets.

Compound[a]	Donor Set[b]	Molecular Skeleton[c]	Ni–N(sp^2)	Ni–O(sp^2)	Bond Angles[d]	Ring Size	Ref.
Ni(sim)$_2$	N_2O_2	Planar	1.84(4)	1.84(4)	93.8(n.d.)	6	21
Ni(Mesim)$_2$ (α-form)	N_2O_2	Planar	1.92(1)	1.85(1)	93.4(4)	6	22
Ni(Mesim)$_2$ (β-form)	N_2O_2	Non-planar	1.90(6)	1.80(6)	96 (n.d.)	6	23
Ni(Etsim)$_2$	N_2O_2	Stepped	1.92(2)	1.84(2)	90 (1)	6	24
Ni(PrMesim)$_2$	N_2O_2	Stepped ($\phi = 16.2°$, $S = 0.76$ Å)	1.920(3)	1.837(2)	92.2(1)	6	25
Ni(Phsim)$_2$	N_2O_2		1.908(n.d.)	1.825(n.d.)	?	6	26
Ni(Hysim)$_2$	N_2O_2	Stepped ($S = 0.24$ Å); H bridge	1.855(5)	1.843(5)	96 (n.d.)	6	27
Ni(DHA imide)$_2$	N_2O_2	Non-planar ($S \approx 0.20$ Å)	1.832(9)	1.835(7)	93.2(9)	6	28
Ni(tan)$_2$	N_2O_2	Stepped ($\phi = 32.6°$; $S = 1.1$ Å)	1.893(14)	1.851(11)	90.8(5)	6	29
Ni(hmab)$_2$	N_2O_2		1.902(5)	1.822(3)	91.1(2)	6	30
Ni(beam)$_2$	N_2O_2	Stepped ($\phi = 2.0°$, $S = 0.08$ Å)	1.832(8)	1.837(4)	91.4(2)	6	This work
Ni(mipdo)(ipdo)	N_3O	Non-planar; H bridge	1.813(1)–1.880(1)	1.819(1)	83.5(1), 92.7(1)	5,6	20
Ni(bigua)$_2\cdot$Cl$_2\cdot$2H$_2$O	N_4		1.86(3)		90.5(n.d.)	6	31
Ni(pyga)$_2$	N_4	3D	1.895(4)		92.4(2)	6 (boat)	32
Ni(DMP)$_2$	O_4	Planar		1.836(5)	94.6(4)	6	33
Ni(mtaat)$_2$	*cis* O_2S_2			1.891(3)	96.3(1)	6	34
Ni(ftp)$_2$	*cis* O_2S_2			1.863(3)	95.9(1)	6	35

[a] Abbreviated terminology: sim, salicylaldimine; Mesim, N-methylsalicylaldimine; Etsim, N-ethylsalicylaldimine; PrMesim, N-isopropyl-3-methylsalicylaldimine; Phsim, N-phenylsalicyl aldimine; Hysim, N-hydroxysalicylaldimine; DHA imide, 3-(1-iminoethyl)-4-hydroxy-6-methyl-2-pyrone; tan, 1-m-tolylazo-2-naphthol; hmab, 2-hydroxy-4′-methylazobenzene; beam, benzoylbenzamidine; mipdo, 4-methyliminopentane-2,3-dione-3-oxime; ipdo, 4-iminopentane-2,3-dione-3-oxime; bigua, biguanide; pyga, dimethylbis(1-pyrazolyl)gallane; DMP, dipivaloylmethanide; mtaat, monothioacetoacet-*p*-toluidide; ftp, 1,1,1-trifluoro-4-thiolopent-3-en-2-one. [b] The number and type of donor atoms; in symmetrical sets the configurations are *trans* unless specifically stated otherwise. [c] Out-of-plane distortions. A stepped configuration of chelate rings is defined by S, the perpendicular separation of chelate ring mean planes, and ϕ, the angle of such planes with the coordination plane. [d] Intra-chelate bond angles, in degrees.

(4-iminopentane-2,3-dione-3-oximato)nickel(II), Ni(mipdo)(ipdo), where the Ni–N(sp^2) bond measures 1.813 Å in a six-membered ring and 1.880 Å in a five-ring [20].

Unstrained Ni–N(sp^2) and Ni–O(sp^2) distances are then most likely to be found amongst the bidentate ligand complexes with a ring size of six rather than in tetraligand and macrocyclic complexes where the metal-donor atom distances appear to be a compromise between the geometrical constraints imposed by the cyclic ligands and the steric requirements of the metal. The structures of a large number of such square-planar organic chelates of nickel have been studied, in particular *trans*-complexes based on salicylaldimine to which Ni(beam)$_2$ can profitably be compared. In these complexes the donor set consists of two nitrogens and two oxygens in a *trans*-configuration, just as in the case of Ni(beam)$_2$. The least deformed complexes appear to be bis-(salicylaldiminato)nickel(II) and Ni(DHA imide)$_2$. In both cases the N_2O_2 unit is exactly planar, whereas the molecular skeleton shows at most minor deviations from planarity; the intraligand angles are 93.8° and 93.2°, respectively, whereas the angle distortion due to coordination is being dissipated in a similar manner as in Ni(beam)$_2$ with the highest distortion at the nitrogen atom (~ 130°). Other reported values refer to complexes with more definite geometrical strain indications. Therefore, a survey of Table IV, which lists a selection of bond data taken from over eighty square-planar nickel complexes, suggests a distance of about 1.83 Å for both the Ni–N(sp^2) and Ni–O(sp^2) bonds not or almost not perturbed by strain. This result, based on the observations of N_2O_2 donor sets, agrees quite well with the observed 1.836 Å Ni–O(sp^2) bond length in the Ni(DMP)$_2$ complex with an O_4 donor set [33]. Therefore, the Ni–N and Ni–O distances in Ni(beam)$_2$ do not appear to be governed by the particular structural constraints of the delocalized planar ligand system which shows absence of appreciable distortions.

The question whether or not there is multiple-bond character in the nickel–ligand bonds cannot be answered unequivocally on the basis of the present data. However, if we accept Owston's [36] value of 1.18 Å for the covalent radius of Ni(II) there would appear to be almost no bond contraction and consequently no appreciable multiple-bond character and d_π–π^*-back-donation. This is in accordance with the chelating strength of Ni(II) [37]. We thus retain that the π-electrons are more localized in the ligand skeleton of the chelate rings.

The Benzoylbenzamidine Ligand

In the nickel coordination sphere the intrachelate angle N–Ni–O differs by 1.4° from the expected 90° and conforms to other values in non-macrocyclic six-membered chelate rings. The angle is shorter than in cases which are constrained by the requirements of attached groupings, as *e.g.* in salicylaldimines. Owing to the distortion due to coordination, most other bond angles in the chelate rings are considerably distorted from the ideal 120° and range from 128.0° to 125.7° and 121.1° on the average in the *o, m* and *p* positions, respectively, in analogy to other structures such as Ni(DMP)$_2$. The "bite" distance between the oxygen and nitrogen atom in the chelate ring is 2.62 Å in this planar complex, *i.e.* close to similar values in other planar complexes and shorter than in the tetrahedral bis-(*N*-isopropylsalicylaldiminato)nickel (II) (2.836 Å) [38], which is again shorter than the 2.913 Å observed in the octahedral diaquobis-(salicylaldehydato)nickel(II) [39].

The bond distances found in Ni(beam)$_2$ indicate electron delocalization within the ligands. In this respect, we notice that the C–O distance is intermediate between single and double bonding. The nitrogen–carbon bond distances (1.35 Å for N(1)–C(1) and N(1)–C(2) and 1.29 Å for N(2)–C(2)) merit special comment. Recent work has established that coordinated C=N lies in the range of 1.29–1.34 Å, whereas coordinated C–N is in the range 1.44–1.51 Å [40–42]. In fact, the longer distance in Ni(beam)$_2$ is reasonably close to those observed in biacetylbis-(mercaptoethylimino)nickel(II) (av. 1.34 Å) [43], falls within the range of carbon–nitrogen bonds in amides (C–N = 1.315–1.385, *cf.* ref. [44]) and is close to pyridine (C–N = 1.34 Å) [45]; the shorter bond distance is only slightly longer than the localized double C–N bond of 1.247(15) Å in bis-(thiosemicarbazidato)nickel(II) [46]. The values reported correspond to bond orders of 1.57 and 1.91 on the Lofthus scale [47]. The difference of 0.06 Å between the bond lengths of the C–N bonds is related to differences between the environments of the two N atoms in that N(2) is involved in a coordinate bond. One may actually expect an asymmetric electronic structure of the chelate ring as a consequence of the two coordinate bonds.

Electron delocalization extends also to the attached phenyl rings. The bonds linking the central rings to the phenyl groups (1.50 Å) are within 3σ to the standard C(sp^2)–C(sp^2) bond length of 1.477 Å [48, 49] and within the range of values (1.486–1.502 Å) observed in quaterphenyl [50] and close to that in biphenyl (1.496 Å) [51]. The C–C bond lengths in the two phenyl rings are in the range 1.368–1.407 Å, which is satisfactorily close (to within 3σ) to the 1.398 Å expected value; the deviation from the latter value may be because we have not attempted to apply a correction for libration to a molecule which seems unlikely to be a rigid body. There are no significant deviations from the values of a regular hexagon. The phenyl groups are planar within the limits of error and the exocyclic bonds are in-plane; the equations for various mean least-squares planes are reported in

TABLE V. Coefficients of Least-squares Plane Equations.[a]

Plane	l	m	n	p	σ^b	Atoms Defining the Plane
A – Coordination	−0.3999	−0.5637	+0.7227	+5.3117	–	Ni N(2) O
B – Ligand	−0.3933	−0.5921	+0.7034	+5.4217	0.03	O C(1) N(1) C(2) N(2)
C – Chelate	−0.3908	−0.5851	+0.7106	+5.3544	0.03	O C(1) N(1) C(2) N(2) Ni
D – Benzene I	−0.3420	−0.5449	+0.7656	+4.6184	0.01	C(3)–C(8)
E – Benzene II	−0.3018	−0.5942	+0.7455	+4.2788	0.02	C(9)–C(14)

Interplanar angles: A–B 2.0°; C–D 4.8°; C–E 5.5°; D–E 3.8°.

[a] Each plane is represented by an equation of the type $lx + my + nz - p = 0$, referred to an orthogonal system of axes with x along the a^* axis, y in the (b–c) plane and z along the c axis; p is the origin-to-plane distance in Å. [b] Root mean-square deviation in Å.

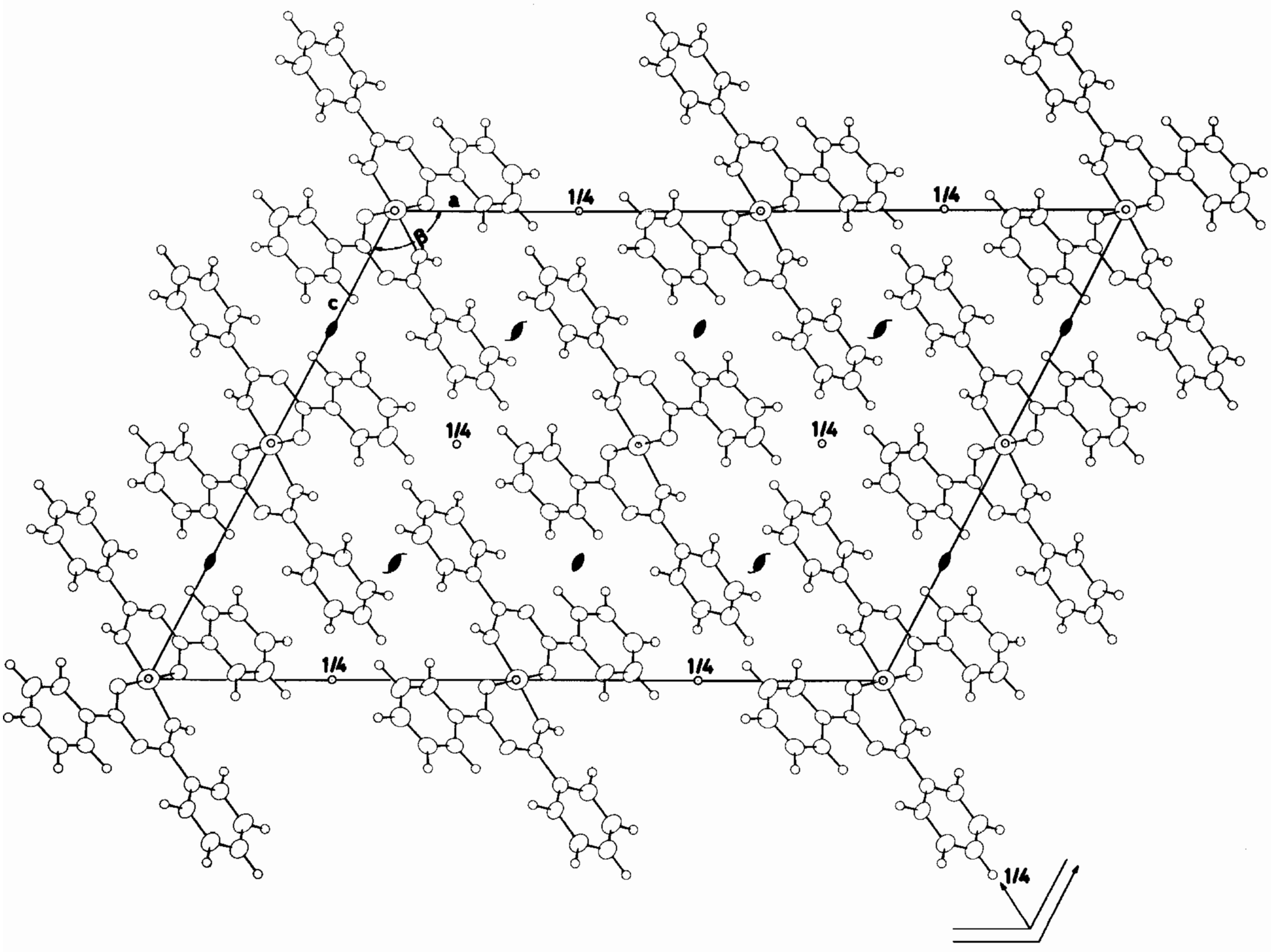

Fig. 3. Packing arrangement of bis-(benzoylbenzamidine)nickel(II) molecules as viewed down the b-axis of the unit-cell.

Table V. No atom falls more than three standard deviations out of the "best" plane it helps to define. The interplanar angles between the chelate ring and the phenyl groups are 4.8° and 5.5°; torsion angles are given in Table III. It is of interest to notice the stepping parameters, as defined in Table IV: $\phi = 2.0^\circ$ and S = 0.08 Å, confirming once more that the residual strain in the ligand is not sufficient to induce deformations from the ideal stereochemistry around the metal ion.

The conformation of the molecule is then a result of the equilibrium of two opposed effects: π-electron delocalisation which tends to coplanar rings and repulsion of aromatic hydrogen atoms and lone electron pairs in the *ortho* positions of the adjacent chelate rings, which would induce deviations from planarity. For an evaluation of such effects we notice the values for the interplanar angles in polyphenylbenzene derivatives (twist around the exocyclic bonds) in the crystalline state, which are: biphenyl, 0° [52–54]; *p*-terphenyl, 0.5° (dynamic disorder at room temperature) [51], 15–27° (order at 113 °K) [55]; 4-bromo, 4′-cyanobiphenyl, 38° [56]; quaterphenyl, 0–1° (dynamic disorder; in fact 11°) [50]; other polyphenyls, 36–40° [57]. The repulsion forces bring about in-plane steric deformations of the *ortho* hydrogen atoms H and H(8), leading to a 2.02(4) Å non-bonded distance, *i.e.* significantly less than 2.34 Å, which is twice the Van der Waals radius for hydrogen in the "hard sphere" approximation [58]. The resultant of these main effects together with the eventually weak crystal packing forces leads to the observed torsion around the exocyclic C–C bonds and distortion of the Ni–N(2)–H angle to 111° and of C(3)–C(8)–H(8) to 126°. However, in so doing, H is now only at 2.33 Å from O′, *i.e.* closer than 2.6 Å, the sum of the Van der Waals radii. On the other hand, the close H––H(8) contact is not sufficient to cause distortion from square-planar configuration towards a tetrahedrally coordinated species. Other significant non-bonded distances are listed in Table III.

In summary, the strain energy in Ni(beam)$_2$ would seem not to be very large. This conclusion is supported by the ease of formation of the compound.

Crystal Structure

Fig. 3 illustrates the packing of the molecules. The molecular plane is tilted some 54.2° out of the (010) plane. There are no unusually close intermolecular approaches and thus the crystal is held together primarily by Van der Waals forces. Only seven independent intermolecular contacts were found to be slightly below the sum of the Van der Waals radii (C, 1.8; Ni, 1.65; N, 1.6; O, 1.4; H, 1.2 Å), namely one H––H distance (2.35 Å), three C––H distances (2.84–2.96 Å) and one C––N, C––C and C––Ni contact at 3.38, 3.46 and 3.40 Å, resp. It is worthwhile noticing that there is no indication of short nickel–nickel distances in the complex (*cf.* ref. [59]), such as there is in the crystals of nickel-dimethylglyoxime [60], bis-(1,2-benzochinondioximato)nickel(II) [61], Ni$_2$(dpt)$_4$ [62] and Ni(DHA imide)$_2$ [28].

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