Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, U.S.A.

The Crystal and Molecular Structure of the Electron Transfer Complex Butane-2, 3-Dione-Bis(2'-Pyridylhydrazonato)Nickel, [Ni(BDPH)-2H]

R. J. Olcott[1] and R. H. Holm

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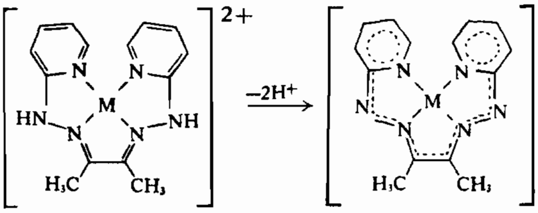
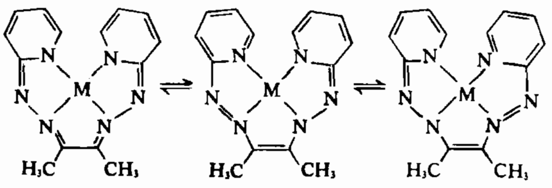
The neutral complex butane-2,3-dione-bis(2'-pyridylhydrazonato)nickel, [Ni(BDPH)–2H], obtained by deprotonation of butane-2,3-dione-bis(2'-pyridylhydrazono)nickel(II) cation, $Ni(BDPH)^{2+}$, crystallizes in the monoclinic $P2_1/c$ space group with four molecules in a unit cell of dimensions a = *16.278(20)* Å, b = *11.891(21)* Å, c = *6.934(12)* Å, β = *91.56(18)*°. *The crystal structure of this compound has been determined by a single crystal X-ray diffraction study. Of the total of 2023 reflections measured by a scintillation counter technique, 1107 showed intensities significantly different from background, and the structure has been refined with these to a weighted R-value of 9.7%. The individual molecules are essentially planar with a trapezoid of donor nitrogen atoms at average distances of 1.828 and 1.939 Å from the metal. The crystal contains stacked columns of parallel molecules in which each nickel experiences two very weak intermolecular Ni . . . N interactions at 3.48 Å roughly normal to the molecular plane. The molecules depart from C_{2v} symmetry, apparently because of packing effects and intermolecular interactions. The patterns of bond distances in the two halves of the ligand are indicative of considerable electron delocalization in each. The delocalized halves are separated by a C–C bridge bond of length 1.53 Å. Although [Ni(BDPH)–2H] has been shown to be the central member of a five-membered electron transfer series, the observed bond distances do not indicate that a simple valence bond description of the ground state electronic structure, proposed for other electron transfer complexes of equivalent oxidation level, is applicable to this molecule, at least the crystalline state.*

Introduction

In the course of our investigations of electron transfer series formed by complexes containing delocalized five-membered chelate rings and metals coordinated wholly[2] or in part by nitrogen,[3,4] we have become interested in species formed from butane-2,3-dione-bis(2'-pyridylhydrazone). This molecule functions as a tetradentate ligand toward divalent metal ions generating the cation complexes *1*.[5,6] Of particular interest are the double-deprotonation reactions of *1* which afford the neutral complexes *2*[6] with potentially delocalized electronic structures. The reaction *1*→*2* is one of numerous deprotonation reactions now known for coordinated ligands containing the 2'-pyridylhydrazone residue.[7] [M(BDPH)–2H] species were originally depicted[6] in terms of the valence bond structure *3*; in addition the equivalent resonance forms *4* and *5*, *among others*, represent possible contributors to the ground state electronic structure. The latter two forms are analogous to those (*6*, *7*) of, *e.g.*, the $M(C_6H_4XY)_2$ group of complexes (X = Y = NH;[2] X = S, Y = NH;[3] X = Y = S[8]), all members of



1 $M(BDPH)^{2+}$ *2* [M(BDPH)–2H]



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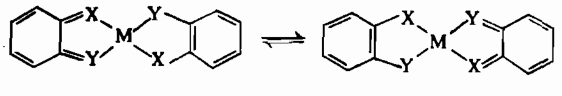
(1) National Science Foundation Predoctoral Fellow, 1966-'68; present address: Department of Chemistry, Southwestern at Memphis, Memphis, Tenn.
(2) A. L. Balch and R. H. Holm, *J. Am. Chem. Soc.*, *88*, 5201 (1966).
(3) A. H. Maki, T. E. Berry, A. Davison, R. H. Holm, and A. L. Balch, *ibid.*, *88*, 1080 (1966).
(4) R. H. Holm, A. L. Balch, A. Davison, A. H. Maki, and T. E. Berry, *ibid.*, *89*, 2866 (1967).
(5) F. Lions and K. V. Martin, *ibid.*, *80*, 3858 (1968).
(6) B. Chiswell and F. Lions, *Inorg. Chem.*, *3*, 490 (1964).
(7) B. Chiswell, F. Lions, and M. L. Tomlinson, *ibid.*, *3*, 492 (1964); R. W. Green, P. S. Hallman, and F. Lions, *ibid.*, *3*, 1541 (1964); C. F. Bell and D. R. Rose, *ibid.*, *7*, 325 (1968); B. Chiswell, *Austr. J. Chem.*, *21*, 1997, 2561 (1968); B. Chiswell and F. Lions, *ibid.*, *22*, 71 (1969).
(8) (a) J. A. McCleverty, *Prog. Inorg. Chem.*, *10*, 49 (1968); (b) G. N. Schrauzer, *Transition Metal Chem.*, *4*, 299 (1968); *Accounts Chem. Res.*, *2*, 72 (1969).

which are known to undergo a series of single electron transfer reactions.[8a] The species [M(BDPH)–2H]^z and M[$C_6H_4(NH)_2$]$_2^z$ (M = Ni, Pd, z = 0) are closely related in the sense that they are the central members of five-membered electron transfer series with components having z = –2, –1, 0, +1, +2.[2,9] All five members of the [Pd(BDPH)–2H]^z series and four of the five members of the [Ni(BDPH)–2H]^z series have been detected polarographically.[9]



In order to establish the structural and certain of the electronic features of members of the [M(BDPH)–2H]^z electron transfer series, we report here the crystal and molecular structure of the central member of the nickel series, [Ni(BDPH)–2H]^0. The detailed structures of two related electron transfer complexes possessing a similar level of oxidation, [$NiS_4C_4Ph_4$]^0 [10] and Ni[$C_6H_4(NH)_2$]$_2^0$,[11] are known. Some structural comparisons are made with the latter.

Experimental Section

Preparation and Crystal Data. Butane-2,3-dione-bis-(2′-pyridylhydrazonato)nickel (2, M = Ni), $C_{14}H_{14}N_6Ni$, was prepared by method (D) of Chiswell and Lions.[6] Numerous recrystallization attempts persistently afforded crystals in the form of parallel aggregates of black needles or slabs intermixed with a small number of apparent single crystals, all of which evidenced internal disorder in Laué photographs. Eventually a very small crystal in the form of a hexagonal prism (0.07×0.08×0.09 mm) was obtained by crystallization from a solution obtained by very slow Soxhlet extraction of the solid with benzene. This crystal showed a clean Laué pattern even after long exposure and was used in the structural investigation. Chemical identity of the disordered and single crystals was verified from zero- and upper-level Weissenberg photographs.

Weissenberg and Buerger photographs of the crystal displayed systematic absences indexable as $0k0$ ($k = 2n$) and $h0l$ ($l = 2n$), indicating space group $P2_1/c = C_{2h}^5$. Unit cell dimensions, obtained from 2Θ measurements of 15 reflections carefully centered on the detection window of a General Electric manual diffractometer using Cu $K_{\bar{\alpha}}$ radiation (1.5418 Å) were determined to be the following: a = 16.278(20), b = 11.891(21), c = 6.934(12) Å, β = 91.56(18)°, and V = 1341.7(37) Å,^{3} where the figures in parentheses are the e.s.d.'s of the final digits. The density was 1.598±0.006 g/cm^3 measured by flotation in dibromoethane-carbon tetrachloride mixtures calibrated by pycnometry. This value compares well with the calculated density of 1.608 g/cm^3 for Z = 4, indicating all molecules in general positions. The 6.9 Å c-dimension, combined with the expected planarity of the molecule, further implied that the molecules occur in two stacks parallel to the c-axis.

Intensity data were obtained from the crystal mounted with the c^*-axis along the Φ axis of a General Electric XRD–5 Spectrogoniometer using Ni-filtered Cu $K_{\bar{\alpha}}$ radiation. Each reflection was preceded by a 10 sec. background count at $2\Theta_{calc}$ –1.67°, the peak scannned at 2°/min. to $2\Theta_{calc}$ +1.67°, and another 10 sec. background taken. In each case a trace of count rate *vs.* time showed that the peak was entirely covered by the scan. Data were taken on 2023 independent reflections out to 2Θ = 120°, of which 1107 possessed intensities more than two standard deviations above background. Detector linearity was checked by remeasuring the 12 strongest reflections at a reduced X-ray tube current (8 ma, *vs.* 15 ma at 45 kVP used for the collected data) and no significant deviation in relative intensities was seen. Instrumental drift and crystal degradation over the 11 day data collection period were estimated by monitoring the measured intensity of the 110 reflection at 2 hr intervals. Over this period the measured peak height of this reflection did not vary significantly, although the measured integrated intensity showed an overall decreasing trend amounting to roughly 3% of the total count. This decrease was observed to correlate with a narrowing of the intensity *vs.* 2Θ curve, indicating that the source of the variation was probably X-ray annealing of the crystal rather than actual degradation. Because the scatter range of individual integrated intensities included about 75% of the overall variation, the data were not corrected for this effect. The measured intensities were corrected for Lorentz and polarization effects, and then for absorption[12] (μ = 21.2 cm^{-1}).

Solution and Refinement of the Structure. The position of the nickel atom in the asymmetric unit, immediately available from the peak positions in the Harker section (u, v, w = 2x, 1/2, 1/2 + 2z) and the Harker line (u, v, w = 0, 1/2+2y, 1/2) in the Patterson map, was refined on F by one cycle of least squares treatment,[13] and the resulting coordinates used to calculate a three-dimensional Fourier synthesis, sectioned parallel to the c-axis. All non-hydrogen atoms were readily discernible in reasonable positions. After four cycles of full matrix isotropic refinement the weighted[14] R factor $\{\Sigma w(|F_o|-$

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(9) O. A. Gansow, R. J. Olcott, and R. H. Holm, *J. Am. Chem. Soc.*, *89*, 5470 (1967).

(10) D. Sartain and M. R. Truter, *J. Chem. Soc.*, *A*, 1264 (1967).

(11) G. S. Hall and R. H. Soderberg, *Inorg. Chem.*, *7*, 2300 (1968).

(12) Computations for this investigation were performed on an IBM 360/65 computer system using the following programs: MIXG2 (D. P. Shoemaker) for calculation of diffractometer settings; PMMO (M. J. Bennett) for reduction of the measured intensity data to $|F_{hkl}|$ and calculation of the corresponding standard deviations; GONO9 (W. C. Hamilton, with local modifications) for correction of the F's for absorption effects; FORDAP (A. Zalkin) for preparation of the Patterson, Fourier, and difference Fourier function maps; SFLS5 (C. T. Prewitt, with local modifications) for least-squares parameter refinement; MGEOM (J. S. Wood) for calculation of bond lengths and angles with standard deviations, and least-squares best planes; PUBTAB (R. C. Elder) for printing structure factors in publication format; ORTEP (C. K. Johnson) for calculation of intermolecular distances and thermal elipsoids, and computer plotting of structure diagrams.

(13) Atomic form factors used were the tabulated functions for C, N, and Ni(II) given by D. T. Cromer and J. T. Waber, *Acta Cryst.*, *18*, 104 (1965), linearly interpolated as necessary for intervals of sinΘ/λ = 0.05.

$|F_c|)^2/\Sigma wF_o^2\}^{1/2}$ had decreased to 13.5%. Correction for anomalous scattering by the nickel atom[15] was initiated and after three additional cycles the weighted R factor was 11.7%; no parameter changed by more than half its standard deviation. A distance-angle calculation on the structure at this point showed a significant departure from the idealized C_{2v} symmetry of *2* arising mainly from the positions of atoms N–11 and C–16 or their counterparts (*cf.* Figure 1). On the possibility that the refinement had converged to a false minimum, these atoms were shifted to sites which would preserve the idealized symmetry and the altered structure refined by two cycles. The resulting structure did not deviate from the original asymmetric one.

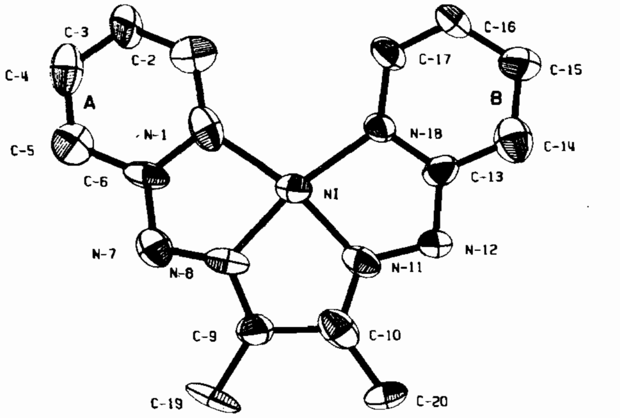

Figure 1. A perspective drawing of the [Ni(BDPH)–2H] molecule with atom labels.

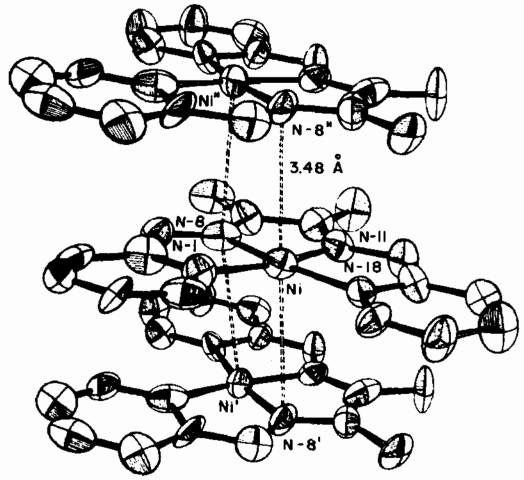

Figure 2. A perspective view of the molecules within a column.

A model of the unit cell at this point in the refinement revealed the packing to be that shown in Figures 2 and 3 with stacks of molecules interrelated by the *c*-glide operation. On the basis of packing interactions the atoms judged most likely to have significant thermal anisotropy were C–15, C–16, C–19, and C–20. Two cycles of refinement with these four and the nickel atom anisotropic reduced the weighted R factor to 10.6%. A difference Fourier synthesis calculated using these parameters showed no peaks of density greater than 0.9 electron/Å^3 but only five peaks of any size at or near reasonable positions for hydrogen atoms. Further, the difference map showed no evidence of steep gradients through the positions assigned to C–3, N–8, N–11, or C–16, indicating that these are the correct placements.

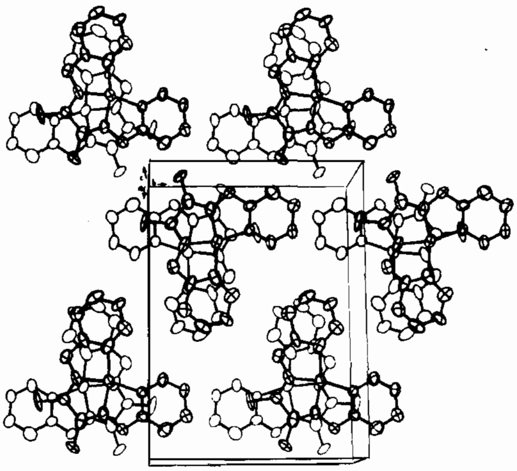

Figure 3. A perspective view of the contents and near environment of a unit cell.

Four cycles of refinement with all atoms allowed to vibrate anisotropically gave a converged structure with a weighted R of 9.7%.[16] This is a significant improvement over the five anisotropic atom model at the 1% level, as shown by an R-value ratio of 1.093 compared to the Hamilton R-test value of 1.068.[17]

The final set of observed and calculated structure factors is given in Table I. The final unweighted R factor, $\Sigma||F_o|-|F_c||/\Sigma|F_o|$, is 11.1% over 1095 reflections, while the final weighted R factor is 9.7% and the estimated standard deviation of a single observation is 2.059. Final atomic coordinates and anisotropic thermal parameters are set out in Table II.

Results and Discussion

Intramolecular bond distances and angles and selected intermolecular distances and angles are given

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(14) All terms were weighted by $w = 1/\sigma^2$, where $\sigma^2 = I_p + (T_p/T_b)^2 I_b$ is the standard deviation of a net intensity I derived from an integrated intensity I_p scanned for T_p sec. and a total background count I_b. The validity of this scheme is supported by the fact that there are no significant trends in a plot of the final values of $w(|F_o|-|F_c|)^2$ vs. $\sin\Theta/\lambda$.

(15) Anomalous scattering corrections were made to the Ni form factors by takin $f = f_{tab} - 3.1 + 0.6i$; *cf.* M. J. Buerger, « Crystal Structure Analysis », John Wiley and Sons, Inc., New York, 1960, pp. 542-547.

(16) Because of the small size of the crystal and the resulting weak X-ray intensities, it was not felt advisable to include the non-significant reflections in the refinement or calculation of the final R values or standard deviations.

(17) W. C. Hamilton, *Acta Cryst.*, *18*, 502 (1965).

Table I. Observed and Calculated Structure Factor Amplitudes (in electrons × 10)

Table II. Final Atomic Coordinates[a, b] and Anisotropic Thermal Parameters[b, c]

Atom	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
N—1	0.6095(8)	0.6942(12)	0.1147(17)	0.0051(7)	0.0063(12)	0.0188(34)	0.0018(9)	−0.0008(12)	0.0012(19)
C—2	0.5490(11)	0.6144(14)	0.1405(21)	0.0047(10)	0.0088(16)	0.0113(40)	−0.0015(10)	0.0005(16)	0.0013(20)
C—3	0.4699(9)	0.6412(14)	0.1688(23)	0.0040(8)	0.0074(16)	0.0191(47)	0.0018(9)	0.0024(15)	−0.0053(21)
C—4	0.4448(10)	0.7515(17)	0.1677(23)	0.0041(8)	0.0111(19)	0.0160(46)	0.0027(11)	−0.0003(14)	−0.0026(27)
C—5	0.4999(11)	0.8372(15)	0.1318(22)	0.0046(9)	0.0079(20)	0.0182(45)	0.0002(11)	0.0006(16)	−0.0063(24)
C—6	0.5868(10)	0.8070(14)	0.1097(22)	0.0053(9)	0.0045(13)	0.0216(46)	−0.0017(10)	0.0013(16)	0.0054(23)
N—7	0.6427(9)	0.8897(10)	0.0939(19)	0.0043(7)	0.0057(11)	0.0209(40)	0.0006(7)	0.0003(13)	−0.0018(17)
N—8	0.7166(9)	0.8393(9)	0.0747(18)	0.0048(7)	0.0042(12)	0.0172(31)	−0.0020(8)	0.0003(12)	0.0008(17)
C—9	0.7876(10)	0.8982(12)	0.0598(23)	0.0029(7)	0.0059(14)	0.0260(50)	−0.0009(8)	−0.0012(15)	0.0023(20)
C—10	0.8616(10)	0.8193(16)	0.0416(21)	0.0059(10)	0.0056(14)	0.0186(43)	0.0007(12)	0.0008(16)	0.0031(24)
N—11	0.8370(8)	0.7148(10)	0.0490(18)	0.0041(6)	0.0041(12)	0.0181(36)	−0.0002(7)	−0.0013(12)	0.0029(15)
N—12	0.8910(7)	0.6247(10)	0.0303(20)	0.0026(6)	0.0045(10)	0.0327(46)	−0.0007(8)	0.0007(13)	0.0001(18)
C—13	0.8469(9)	0.5288(13)	0.0407(22)	0.0024(7)	0.0062(14)	0.0232(47)	−0.0003(9)	−0.0001(14)	0.0046(20)
C—14	0.8920(10)	0.4240(14)	0.0351(24)	0.0044(8)	0.0085(16)	0.0232(49)	0.0012(10)	−0.0013(15)	−0.0007(22)
C—15	0.8470(10)	0.3245(16)	0.0441(26)	0.0041(8)	0.0058(14)	0.0420(60)	−0.0008(11)	0.0006(17)	0.0022(28)
C—16	0.7594(9)	0.3326(14)	0.0625(25)	0.0043(8)	0.0038(16)	0.0371(54)	0.0002(9)	0.0003(17)	−0.0027(26)
C—17	0.7228(10)	0.4333(11)	0.0709(25)	0.0042(7)	0.0040(11)	0.0238(44)	0.0002(10)	−0.0003(13)	−0.0032(23)
N—18	0.7641(7)	0.5321(9)	0.0618(17)	0.0024(6)	0.0038(10)	0.0223(36)	−0.0002(6)	−0.0021(11)	−0.0020(15)
C—19	0.7941(11)	1.0214(12)	0.0546(24)	0.0084(11)	0.0026(11)	0.0277(53)	−0.0024(9)	−0.0019(19)	0.0023(20)
C—20	0.9480(9)	0.8587(13)	0.0210(28)	0.0029(7)	0.0067(14)	0.0495(68)	−0.0024(9)	0.0015(18)	−0.0010(25)
Ni	0.7273(2)	0.6864(2)	0.0742(2)	0.0032(1)	0.0046(2)	0.0182(6)	−0.0008(2)	−0.0002(2)	0.0001(3)

[a] Unit cell edge fractions; [b] estimated standard deviations in least significant digits; [c] the form of the anisotropic thermal ellipsoid is given by $\exp[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+2b_{12}hk+2b_{13}hl+2b_{23}kl)]$

Table III. Interatomic Distances (Å)[a]

Atoms	Distance	Atoms	Distance
N—1, C—2	1.38(2)	N—18, C—17	1.36(2)
C—2, C—3	1.34(2)	C—17, C—16	1.34(2)
C—3, C—4	1.37(3)	C—16, C—15	1.44(2)
C—4, C—5	1.38(3)	C—15, C—14	1.39(2)
C—5, C—6	1.47(3)	C—14, C—13	1.45(2)
C—6, N—1	1.39(2)	C—13, N—18	1.36(2)
C—6, N—7	1.35(2)	C—13, N—12	1.35(2)
N—7, N—8	1.35(2)	N—12, N—11	1.39(2)
N—8, C—9	1.36(2)	N—11, C—10	1.31(2)
C—9, C—19	1.47(2)	C—10, C—20	1.49(2)
N—1, Ni	1.945(14)	N—18, Ni	1.933(11)
N—8, Ni	1.827(11)	N—11, Ni	1.829(13)
N—1, N—8	2.49(2)	N—18, N—11	2.48(2)
N—1, N—18	3.20(2)	N—8, N—11	2.48(2)
C—9, C—10	1.53(2)	Ni, N—8′[b]	3.478(13)

[a] Estimated standard deviations in least significant digits in parentheses; [b] intermolecular distance (cf. Figure 2).

Table IV. Bond Angles (deg)[a]

Atoms[b]	Angle	Atoms[b]	Angle
N—1, Ni, N—8	81.8(6)	N—11, Ni, N—18	82.4(5)
N—1, Ni, N—18	111.0(5)	N—8, Ni, N—11	84.8(6)
N—1, Ni, N—8′	96.8(5)	N—18, Ni, N—8′	83.2(4)
N—8, Ni, N—8′	95.0(4)	N—11, Ni, N—8′	87.1(5)
N—8′, Ni, N—8″	168.4(5)	Ni, N—8, Ni″	84.9(5)
N—1, C—2, C—3	123(2)	N—18, C—17, C—16	123(2)
C—2, C—3, C—4	121(1)	C—17, C—16, C—15	120(2)
C—3, C—4, C—5	121(2)	C—16, C—15, C—14	118(2)
C—4, C—5, C—6	118(1)	C—15, C—14, C—13	118(1)
C—5, C—6, N—1	119(1)	C—14, C—13, N—18	122(1)
C—6, N—1, C—2	118(2)	C—13, N—18, C—17	118(1)
Ni, N—1, C—6	108(1)	Ni, N—18, C—13	110(1)
N—1, C—6, N—7	122(1)	N—18, C—13, N—12	121(1)
C—6, N—7, N—8	107(1)	C—13, N—12, N—11	108(1)
N—7, N—8, Ni	122(1)	N—12, N—11, Ni	119(1)
Ni, N—8, C—9	116(1)	Ni, N—11, C—10	119(1)
N—8, C—9, C—10	111(1)	N—11, C—10, C—9	110(1)
N—8, C—9, C—19	125(1)	N—11, C—10, C—20	126(1)

[a] Estimated standard deviations of least significant digits in parentheses; [b] angles including primed atoms are intermolecular (*cf.* Figure 2).

in Tables III and IV. Atom numbering of an individual molecule is indicated in Figure 1. The most interesting feature of the crystal structure is the arrangment of molecules in columns along the *c*-axis with the individual mloecular planes roughly parallel to the *ab*-plane. The arrangement of molecules within a column is depicted in Figure 2, and the contents and near environment of a unit cell viewed down the *c**-axis is shown in Figure 3.

The individual molecular structure is essentially planar. The molecule as a whole closely conforms to a plane with the equation $0.1244x''+0.0029y''+0.9922z'' = 2.023$ Å (x'' and y'' along *a* and *b*, z'' normal to the *ab* plane). The largest perpendicular atomic displacement from this least-squares best plane is 0.108 Å (C—3). Further calculations of best planes in the two halves of the molecule defined by a line passing through the nickel atom and bisecting the C–9, C–10 bond revealed a small twist angle of 3.1°, which arises from a very slight tetrahedral distortion. The half containing pyridine ring B is planar within experimental error ($0.0975x''-0.0024y''+0.9952z'' = 1.628(18)$) while small deviations from overall planarity occur in the A half ($0.1187x''+0.0463y''+0.9918z'' = 2.375(49)$). Inspection of the respective direction cosines shows that the B-side plane is essentially normal to the *c*-axis while the A-side plane is tilted with respect to it.

The coordination sphere of four nitrogens very closely approaches a trapezoidal plane with a barely significant (0.025 Å average deviation) tetrahedral distortion. The trapezoid has three sides of length 2.48 Å, defining the bites of the three fused chelate rings, and a fourth side some 0.72 Å longer. The two distances between nickel and the pyridine nitrogens average to 1.94 Å whereas the Ni, N–8 and Ni, N–11 distances average to 1.83 Å, among the shortest Ni–N bonds reported (*vide infra*). The individual molecules depart from strict C_{2v} symmetry. Members of the bond pairs C—3, C—4— —C—16, C—15 and N—8, C—9— —N—11, C—10 and of the angle pair Ni, N—8, C—9— —Ni, N—11, C—10 differ beyond experimental uncertainty. This asymmetry is almost certainly a function of crystalline packing and attendant intermolecular interactions and not an inherent property of the isolated molecule.

Reference to Figures 2 and 3 reveals the existence of two ...Ni...N–8...Ni...N–8... chains of interaction in each column, with these intermolecular distances being 3.48 Å. Within the column the molecules are locked in an alternating quarter-turn sequence, producing an orientation such that pyridine ring B of each molecule overhangs on one side or the other ,of the column, while ring A is interleaved between symmetry-related pyridine rings of superior and inferior molecules. The lack of correspondence, within experimental error, of certain angles and distances involving N–8 and N–11 appears to arise because of the involvement of the former in intermolecular interactions. These are obviously very weak, as judged by the long distance involved, but may be responsible for the low solubility of the compound in non-coordinating solvents. The molecular packing is somewhat similar to that observed in nickel(II) phthalocyanine,[18] in which the perpendicular intermolecular spacing is 3.38 Å and each nickel atom lies above and below a corner-nitrogen, which, however, is not part of the planar coordination sphere. Comparable intermolecular spacings (3.2 - 3.4 Å) have been observed in crystals of other planar bis-chelate nickel(II) complexes of the $Ni–N_4$ type, *viz.*, several bis(glyoximato) species, [19-21] but in no case are specific Ni...N interactions evident.

Returning to the structure of an individual molecule, certain of the observed distances are indicative of considerable electron delocalization. The C—6, N—7, N—7,N—8, C—13,N—12, and N—12, N—11 distances are intermediate between reasonable limiting values for single and double bonds.[22] In particular, the N–N distances are shorter than the N–N single bonds in the five-membered chelate rings of the α– and β–modifications of bis(thiosemicarbizido)nickel(II) sulfate[23] (av. 1.43 Å) and much shorter than the corresponding distance (1.54 Å) in bis(thiosemicarbizidato)nickel(II).[24] The average value of 1.35 Å found in 3-ethoxy-2-oxobutyraldehydebis(thiosemicarbazonato)copper(II)[25] (Cu–KTS), which, like [Ni(BDPH)–2H], contains three fused, conjugated, five-membered chelate rings, is fairly close to that observed here. The C–N bond lengths are comparable with those of bis(thiosemicarbazido)nickel(II) cation and Cu–KTS (av. 1.33 Å) but longer than the 1.25 Å value observed in bis(thiosemicarbazidato)-nickel(II). An appropriate lower limit for a C–N single bond of this type can presumably be taken as 1.44 Å, the smaller of two C–N distances found in the saturated five-membered chelate rings of biacetylbis(mercaptoethylimino)nickel(II).[26] Delocalization also extends to C–9 and C–10. The N–8, C–9 bond might be slightly elongated by packing effects and intermolecular interactions. The two C–N distances are reasonably close to those observed in Cu–KTS (av. 1.30 Å) and biacetylbis(mercaptoethylimino)nickel(II) (av. 1.34 Å). However, the C–9, C–10 bond (1.53 Å) is surprisingly long compared to those of the latter complex and Cu–KTS which are 1.44 and 1.47 Å, respectively. The bond length patterns in the pyridine rings cannot be accounted for in detail and the cause of the relatively long C–5, C–6 and C–14, C–13 distances is unknown. Other distances deviate from those in pyridine itself[27] (C–N 1.34, C–C 1.39 Å). The results point to two delocalized π-systems extending over the 2′-pyridyl

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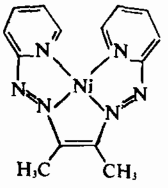
groups, the atoms C–6, N–7, N–8, C–9, and their counterparts, which are effectively separated by the long C–C bridge bond whose distance is essentially that of a C–C single bond.

The nickel-nitrogen distances are set to a considerable extent by the structural constraints of the delocalized planar ligand system which appears to require, in the absence of appreciable distortions of its bond angles and distances, a trapezoidal coordination sphere. Hence, the significance of the two sets of Ni–N distances in terms of a possible shortening due to the overall oxidation level of the molecule is difficult to assess,[28] a matter which requires structural data, presently unavailable, on other oxidized or reduced members of the [Ni(BDPH)–2H]^z electron transfer series. At present we can only point out that the average distances of 1.83 Å for two of the Ni–N bonds is the same as the average Ni–N distance in Ni[$C_6H_4(NH)_2$]$_2$,[11] which, like [Ni(BDPH)–2H], is the central member of a five-membered eletcron transfer series[2] and thus possess an equivalent level of oxidation. This distance is 1.82 Å in diacetyl–dihydro–bis(2–mercaptoanil)nickel monoanion,[29] which has electron transfer potentiality. It is further noted that Ni–N distances in the range 1.83-1.88Å have been observed for three bis(glyoximato)nickel(II) complexes[19-21] in which neither metal nor ligands possess unambiguous formal oxidation states. Hence the Ni-N distance of 1.83 Å observed in [Ni(BDPH)–2H] cannot be taken on face value as abnormally short and may in fact be reasonably typical of that expected for nickel(II) coordinated to an α-diimine residue.

The most significant structural feature of [Ni(BDPH)–2H], other than its planarity, is the long C-9, C-10 bridge bond which signifies little, if any, π-interaction of the delocalized halves of the entire ligand system through this point of attachment. In terms of a simple valence bond description of electronic structures, the forms *4*$\rightleftharpoons$*5* can make no important contribution for they require a considerably shorter bridge bond than actually observed. This result was not entirely anticipated inasmuch as the forms *6*$\rightleftharpoons$*7* provide a reasonable, simple description of M(C_6H_4-XY)$_2$ and other electron transfer complexes having an oxidation level equivalent to that of [Ni(BDPH)–2H], and the bond lengths of Ni[$C_6H_4(NH)_2$]$_2$[11] are not inconsistent with this description. Further, Cu–KTS is a potential electron transfer complex[30] of corresponding oxidation level and, as mentioned above, possesses a bridge bond some 0.06 Å shorter than that in [Ni(BDPH)–2H]. Also ruled out as important contributors are any formulations such as *8* and *9* which involve, formally, Ni^0 and Ni^{IV}, respectively. It is concluded that none of the simple valence structures *3*, *4*, *5*, *8*, and *9*, alone or in combination, provide a satisfactory description of the molecule, at least in the crystalline state. The formulation *2*, but without the indicated interaction across the C–C bridge, adequately conveys the delocalized electronic structure. Attempts to rationalize the observed ligand bond lengths or average lengths of pairs of corresponding bonds by several types of π-electron molecular orbital calculations on the ligands in the zero to – 4 formal oxidation states have proved indecisive.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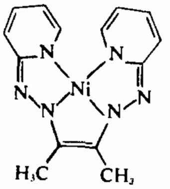
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(28) Note that in the series Ni(mnt)$_2^{2-}$, Ni(mnt)$_2^{-}$, [$NiS_4C_4Ph_4$]^0 a trend of decreasing Ni—S bond lengths is seen as the oxidation level is increased.[8a,10]

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(30) For closely related cases *cf.* ref. 4.