COLELLA, C. (1973). *Rend. Accad. Sci. Fis. Mat.* **40**, 303–313.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
DAVIES, J. E. & GATEHOUSE, B. M. (1973). *Acta Cryst.* B**29**, 1934–1942.
DEER, W. A., HOWIE, R. A. & ZUSSMAN, J. (1963). *Rock-forming Minerals*. Vol. 4. *Framework Silicates*, p. 371. London: Longmans.
HAIDINGER, W. (1825). *Ann. Phys. Lpz.* **5**, 193–198.
HEY, M. H. (1934). *Miner. Mag.* **23**, 483–494.
JONES, J. B. (1968). *Acta Cryst.* B**24**, 355–358.
NORDENSKJÖLD, O. (1895). *Geol. Fören. Stockh. Förh.* **17**, 597.
NOVAK, F. (1970). *Acta Univ. Carolinae, Geol.* pp. 237–251.
STRUNZ, H. (1970). *Mineralogische Tabellen*. 5th ed., p. 487. Leipzig: Akademie-Verlag.
TAYLOR, W. H. (1935). *Miner. Mag.* **24**, 208–220.
TAYLOR, W. H. & JACKSON, R. (1933). *Z. Kristallogr.* **86**, 53–64.
TSCHERMAK, G. (1918). *Sitzungsber. Akad. Wiss. Wien, Math.-Naturwiss. Kl.* **127**, 177–289.
VAN REEUWIJK, L. P. (1972). *Amer. Min.* **57**, 499–510.

Acta Cryst. (1976). B**32**, 1627

The Crystal and Molecular Structure of Bis[dihydrobis-(1-pyrazolyl)borato]nickel(II): Evidence for the Absence of Ni–H Interaction in Polypyrazolyl Borates of Nickel

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(*Received* 2 *September* 1975; *accepted* 7 *November* 1975)

The crystal structure of bis[dihydrobis-(1-pyrazolyl)borato]nickel(II), $[H_2B(C_3N_2H_3)_2]_2Ni^{II}$, has been determined to a reliability index $R=0{\cdot}056$. The space group is *Pbca* with cell parameters $a=6{\cdot}331$ (2), $b=17{\cdot}485$ (7), and $c=14{\cdot}519$ (3) Å. The X-ray structure of this compound supports the recent hypothesis that the methylene H atoms of the bis[diethyl bis-(1-pyrazolyl)borato]nickel(II) complex do not act as apical ligands.

Introduction

Kosky, Ganis & Avitabile (1971) and Cotton, Jeremic & Shaver (1972) have reported an electronic interaction between the central metal and a nearby hydrogen in pyrazolyl borates of molybdenum, resulting in a stable 18-electron configuration and near octahedral geometry. The crystal structure of bis[diethyl bis-(1-pyrazolyl)borato]nickel(II) (Echols & Dennis, 1974) suggested that no such electronic interaction exists in this nickel complex. Although methylene H atoms occupy apical positions near nickel, there was no reason to propose that they were acting as ligands since there was no perturbation of the Ni–N bond lengths from the square planar values of analogous compounds (Nyburg & Wood, 1964). The present structure determination was undertaken to resolve the question of Ni–H interaction. The dihydro derivative serves as an excellent control for the comparison of Ni–N bond lengths.

Experimental

Red-orange crystals of bis[dihydrobis-(1-pyrazolyl)borato]nickel(II), $[H_2B(C_3N_2H_3)_2]_2Ni^{II}$, were provided by Dr S. Trofimenko. Precession photographs showed systematic absences characteristic of the space group *Pbca*: $k=2n+1$ for $0kl$, $l=2n+1$ for $h0l$, and $h=2n+1$ for $hk0$; $h00$, $0k0$, and $00l$ reflections had absences of $h=2n+1$, $k=2n+1$, and $l=2n+1$ respectively.

Unit-cell dimensions (Table 1) were calculated by least-squares refinement of 2θ, ω, and χ settings for 15 independent reflections. Intensity data were collected on a Syntex $P\bar{1}$ computer-controlled diffractometer using molybdenum graphite-monochromatized radiation in the θ–2θ scan mode. Individual scan speeds were determined by a rapid scan at the calculated Bragg peak; the final scan rate varied from 2·0 to 24·0° min^{-1}. Background counts on each side of the peak were counted for $\frac{1}{4}$ the peak scan time. Three reflections were monitored 28 times during the data collection to check alignment and decomposition. Two symmetry equivalent sets of data (hkl and $hk\bar{l}$) were collected; equivalent reflections in these two sets showed no evidence of decomposition or the need for absorp-

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tion corrections. All reflections were corrected for Lorentz and polarization effects, and the two sets of data were averaged. The resulting reflections were assigned observational variances $\sigma(F)$ on the basis of counting statistics for the scan and background. All reflections had $\sin\theta/\lambda \le 0{\cdot}70$. During least-squares refinement, six reflections (002, 020, 111, 113, 200, and 210) were discarded with values of $w^*\Delta F$ much greater than the rest. The first four were large reflections, and their intensities were suspected to have exceeded the linearity of the counter. Atomic scattering factors for

Table 1. *Crystal data*

Molecular formula: $NiN_8B_2C_{12}H_{16}$
M.W. 352·65
Crystal dimensions: 0·4 × 0·35 × 0·3 mm
Space group: *Pbca*
$a = 6{\cdot}331\ (2)$ Å
$b = 17{\cdot}485\ (7)$
$c = 14{\cdot}519\ (3)$
$D_m = 1{\cdot}48$ g cm^{-3}
$D_c = 1{\cdot}458$
$Z = 4$
Radiation: Mo $K\alpha$, $\lambda_{ave} = 0{\cdot}7114$ Å
Number of reflections taken/used: 2336/2302
Set of hkl taken: $+h+k+l$ & $+h-k+l$
Linear absorption coefficient, $\mu = 12{\cdot}36$ cm^{-1}

Table 2. *Positional parameters as fractional coordinates, with standard deviations in parentheses*

	x	*y*	*z*
Ni	0·00000	0·00000	0·00000
N(1)	−0·0326 (4)	0·0965 (1)	−0·0577 (1)
N(2)	−0·0835 (4)	0·1607 (1)	−0·0091 (1)
N(3)	−0·2238 (4)	0·0222 (1)	0·0818 (1)
N(4)	−0·2504 (4)	0·0931 (1)	0·1192 (1)
B	−0·0864 (5)	0·1568 (2)	0·0979 (2)
C(1)	−0·1286 (5)	0·2175 (1)	−0·0680 (2)
C(2)	−0·1104 (6)	0·1904 (2)	−0·1566 (2)
C(3)	−0·0478 (5)	0·1147 (2)	−0·1470 (2)
C(4)	−0·3932 (5)	−0·0198 (2)	0·1065 (2)
C(5)	−0·5296 (5)	0·0247 (2)	0·1598 (2)
C(6)	−0·4316 (4)	0·0950 (2)	0·1658 (2)
H(C1)†	−0·172	0·275	−0·049
H(C2)†	−0·139	0·221	−0·220
H(C3)†	−0·016	0·076	−0·203
H(C4)†	−0·420	−0·079	0·088
H(C5)†	−0·679	0·008	0·190
H(C6)†	−0·492	0·144	0·203
H(B)*	−0·153	0·220	0·116
H′(B)*	0·047	0·142	0·121

* The positions of the hydrogen atoms on boron were located from a difference Fourier map. An estimate of the likely uncertainties in these positions would be approximately three times the uncertainties observed for the boron parameters.

† The positions of the ring hydrogen atoms were calculated.

Table 3. *Thermal parameters* (× 10²) *for the non-hydrogen atoms*

Parameters are in the form $\exp[-2\pi^2\{U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*\}]$. Hydrogen atoms were given an isotropic thermal parameter $U = 0{\cdot}0507$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	4·3 (0)	2·7 (0)	3·2 (0)	0·3 (0)	0·7 (0)	0·3 (0)
N(1)	5·4 (1)	3·4 (1)	3·4 (1)	0·2 (1)	0·6 (1)	0·5 (1)
N(2)	4·9 (1)	3·0 (1)	4·4 (1)	0·3 (1)	0·3 (1)	0·3 (1)
N(3)	4·7 (1)	3·4 (1)	4·0 (1)	0·1 (1)	0·8 (1)	0·3 (1)
N(4)	4·7 (1)	3·7 (1)	3·5 (1)	0·5 (1)	0·5 (1)	−0·1 (1)
B	5·2 (2)	4·0 (1)	4·0 (1)	−0·2 (1)	0·2 (1)	−0·5 (1)
C(1)	6·3 (2)	3·4 (1)	5·7 (2)	0·5 (1)	−0·2 (1)	1·1 (1)
C(2)	7·9 (2)	4·7 (1)	4·8 (1)	0·9 (2)	−0·7 (2)	1·6 (1)
C(3)	6·6 (2)	4·6 (1)	3·7 (1)	−0·4 (1)	0·3 (1)	0·6 (1)
C(4)	4·8 (1)	4·8 (1)	4·4 (1)	−0·5 (1)	0·5 (1)	0·6 (1)
C(5)	4·3 (1)	6·1 (2)	4·6 (1)	0·3 (1)	0·7 (1)	0·9 (1)
C(6)	4·7 (1)	5·3 (1)	3·9 (1)	1·2 (1)	0·8 (1)	0·3 (1)

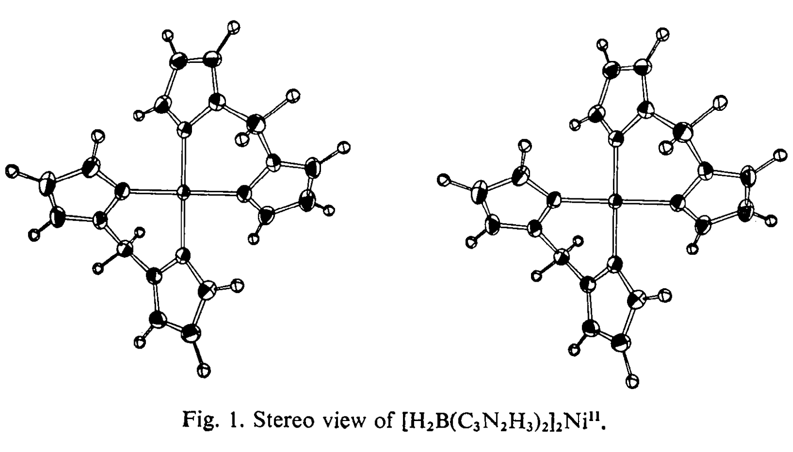

Fig. 1. Stereo view of $[H_2B(C_3N_2H_3)_2]_2Ni^{II}$.

neutral Ni, N, C, B, and H were taken from *International Tables for X-ray Crystallography* (1968).

Determination of the structure and refinement

Patterson synthesis confirmed the nickel atoms at 0,0,0, $\frac{1}{2},\frac{1}{2},0$, $0,\frac{1}{2},\frac{1}{2}$, and $\frac{1}{2},0,\frac{1}{2}$, and showed possible Ni–N vectors. A three-dimensional Fourier synthesis phased on the Ni atom ($R=0{\cdot}45$) revealed the position of the first pyrazolyl ring. These coordinates allowed the calculation of a map ($R=0{\cdot}35$) showing the locations of the N atoms of the second pyrazolyl ring and boron. A Fourier synthesis based on these positions ($R=0{\cdot}28$) located the three remaining C atoms. Inclusion of all the non-hydrogen atoms in the asymmetric unit resulted in an R value of 0·18.

Least-squares refinement of positional and isotropic temperature parameters gave an R of 0·13; the function minimized was $R(F)=\sum w(|F_o|-|F_c|)^2$, where unit weights were chosen for all data throughout the refinement process. The H atoms on boron were difficult to locate accurately from a difference Fourier map. Consequently, the calculated coordinates for all the H atoms were used with assigned isotropic temperature factors of 4·0 Å^2. These H parameters were held fixed while the non-hydrogen parameters were refined anisotropically for two cycles ($R=0{\cdot}068$). At this point, the six reflections with $w^*\Delta F>10{\cdot}0$ ($w=1{\cdot}0$) were removed; three more cycles of anisotropic refinement yielded an R of 0·056. The ring H positions were now recalculated (Table 2), based on the refined non-hydrogen parameters. A difference Fourier map involving all non-hydrogen atoms plus the adjusted ring H coordinates now clearly revealed the positions of the H atoms on boron. A final difference Fourier map from structure factors which included the parameters of all the atoms in the asymmetric unit (Tables 2 and 3) checked the fit of F_c to F_o; the final value of the R index for $w=1{\cdot}0$ was 0·056.* The X-RAY 70 system of programs (Stewart, Kundell & Baldwin, 1970) was used.

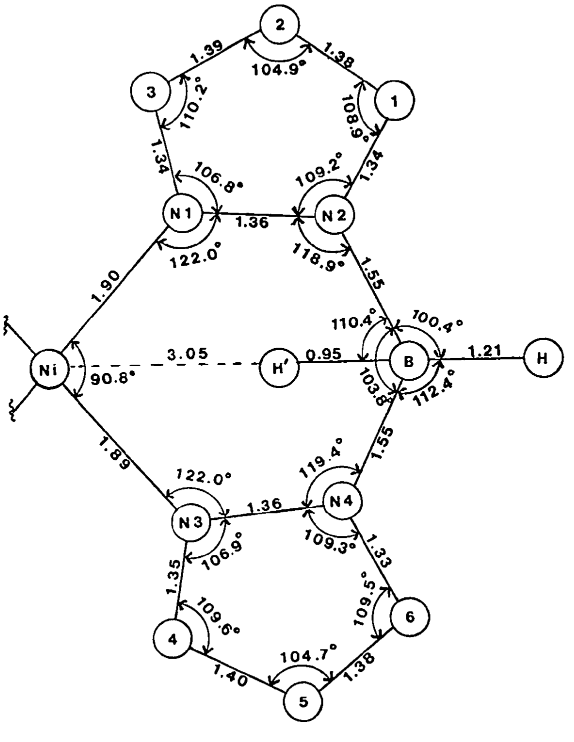

Fig. 2. Numbering of non-hydrogen atoms and hydrogens of interest in $[H_2B(C_3N_2H_3)_2]_2Ni^{II}$.

Description of the structure

The stereochemistry of the complex is depicted in an *ORTEP* drawing in Fig. 1 (Johnson, 1970). The molecular conformation is similar to that reported for bis[diethyl bis-(1-pyrazolyl)borato]nickel(II), and to bis[dimethyl bis-(1-pyrazolyl)gallato]nickel(II) (Rendle, Storr & Trotter, 1974). The planar pyrazolyl rings joined to B create a 'chair' conformation about the inversion center at Ni. The geometry about Ni is square planar. Important planes are given in Table 4. Fig. 2 depicts the approximately tetrahedral geometry about B and the positions of the H atoms relative to Ni. H'(B) is closest, yet still well removed from Ni, with an interatomic distance of 3·05 Å.

Table 4. *Equations of planes, angles between planes, and displacement of atoms from planes*

Plane A: Ni–N(1)–N(3)
$4{\cdot}120X+6{\cdot}990Y+9{\cdot}371Z=0{\cdot}000$
Plane B: B–N(2)–N(4)
$-4{\cdot}614X+11{\cdot}966Y+0{\cdot}307Z=2{\cdot}305$
Plane C: N(1)–N(2)–N(3)–N(4)
$5{\cdot}568X-1{\cdot}158Y+6{\cdot}812Z=-0{\cdot}700$

Displacements from mean plane

N(1)	0·012 Å
N(2)	−0·013
N(3)	−0·012
N(4)	0·013

The X-ray structure of this Ni complex permits a clearer evaluation of the question of electronic interaction between Ni and H in the complex bis[diethyl bis-(1-pyrazolyl)borato]nickel(II). As reported earlier (Echols & Dennis, 1974), the close proximity of the methylene H atom to Ni (2·46 Å) and its apical position might suggest such an interaction. Kosky *et al.* (1971), Cotton *et al.* (1972), and Cotton, La Cour & Stanislowski (1974) have reported such interactions between Mo and H.

In certain complexes, Ni can exist in either a diamagnetic square planar or a paramagnetic octahedral state. The Ni–N bonds increase in length when the

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* The structure factor tables have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31507 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 5. *Comparison of important distances and angles*

	$[H_2B(C_3N_2H_3)_2]_2Ni^{II}$	$[(CH_3CH_2)_2$-$B(C_3N_2H_3)]_2Ni^{II}$
Bond length		
Ni–N(1)	1·895 (2) Å	1·875 (8) Å
Ni–N(3)	1·889 (2)	1·880 (4)
Ni–B	3·136 (2)	3·159 (17)
Dihedral angle		
(A,B)	79·2°	78·4°
(A,C)	31·8	32·5
(B,C)	47·4	45·9

complex converts from diamagnetic (1·89 Å) to paramagnetic (2·0–2·15 Å) (Nyburg & Wood, 1964). Trofimenko, Jesson & Eaton (1967) have shown that the magnetic moment of the title complex is consistent with a diamagnetic square planar structure, and hence it serves as a good control for the comparison of Ni–N bond lengths, seen in Table 5. There are no significant differences in the Ni–N bond lengths for the title complex and the diethyl derivative. The control has very slightly longer Ni–N bonds than its diethyl derivative, not the reverse, as would be expected should a metal–hydrogen interaction exist. A similar Ni–N bond length (1·895 Å) was found by Rendle *et al.* (1974) for square planar $[Me_2Ga(N_2C_3H_3)_2]_2Ni^{II}$. All these complexes have Ni–N distances that are shorter than those found by Reimann, Santoro & Mighell (1970) for the clearly octahedral complex hexapyrazolenickel(II) nitrate, 2·125 Å.

The Ni–B distances give no indication of any interaction; no evidence is seen for the B atom being 'pulled' toward the central Ni atom. This conclusion is supported by a comparison of the dihedral angles for the planes in the two complexes, in Table 5. The largest difference is a 1·5° variation in the angle between the plane B–N(2)–N(4) and the plane N(1)–N(2)–N(3)–N(4). The smaller value (45·9°) for the diethyl derivative indicates that the B–N(2)–N(4) plane is tilted slightly farther away from Ni than is the corresponding plane in the control. Apparently there is no force attracting the methylene H atom of the diethyl complex closer to the central Ni.

It would therefore appear that although an H atom may act as a ligand in other types of metal pyrazolyl complexes, it does not do so when the central metal is nickel. The crystal structure of bis[dihydrobis-(1-pyrazolyl)borato]nickel(II) supports the hypothesis that in the diethyl compound, steric restrictions dictate the conformation of the molecule, not an interaction of Ni with an apical H atom.

We are indebted to Professor T. Kistenmacher, who collected the data and also provided advice throughout the structure determination.

We are most grateful to Dr S. Trofimenko for supplying the crystals and to Dr L. Guggenberger and Dr R. C. Gearhart for helping us obtain the final stereo drawing.

References

Cotton, F. A., Jeremic, M. & Shaver, A. (1972). *Inorg. Chim. Acta*, **6**, 543–551.

Cotton, F. A., La Cour, T. & Stanislowski, A. G. (1974). *J. Amer. Chem. Soc.* **96**, 754–760.

Echols, H. M. & Dennis, D. (1974). *Acta Cryst.* B**30**, 2173–2176.

International Tables for X-ray Crystallography (1968). Vol. III. Birmingham: Kynoch Press.

Johnson, C. K. (1970). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.

Kosky, C. A., Ganis, P. & Avitabile, G. (1971). *Acta Cryst.* B**27**, 1859–1864.

Nyburg, S. C. & Wood, J. S. (1964). *Inorg. Chem.* **3**, 468–476.

Reimann, C. W., Santoro, A. & Mighell, A. D. (1970). *Acta Cryst.* B**26**, 521–526.

Rendle, D. F., Storr, A. & Trotter, J. (1974). *Chem. Commun.* pp. 406–407.

Stewart, J. M., Kundell, F. A. & Baldwin, J. C. (1970). X-RAY 70 System. Computer Science Center, Univ. of Maryland, Cybernet Service, Control Data Corporation.

Trofimenko, S., Jesson, J. P. & Eaton, D. R. (1967). *J. Amer. Chem. Soc.* **89**, 3148–3158.