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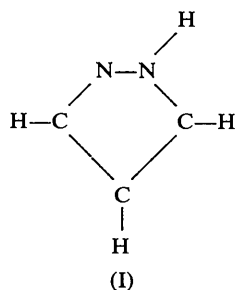
The crystal and molecular structure of dibromotetrapyrazolenickel(II), Ni(C₃H₄N₂)₄Br₂. By A. D. MIGHELL, C. W. REIMANN and A. SANTORO, *Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234, U.S.A.*

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The crystal and molecular structure of dibromotetrapyrazolenickel(II), Ni(C₃H₄N₂)₄Br₂, was determined by single-crystal X-ray diffraction techniques. Ni(C₃H₄N₂)₄Br₂ crystallizes in the monoclinic system with $a = 14.127 \pm 0.007$, $b = 9.334 \pm 0.003$, $c = 14.702 \pm 0.002$ Å, $\beta = 118.62 \pm 0.03^\circ$, space group $C2/c$, $\rho = 1.94$ g.cm⁻³ and $Z = 4$. The structure was found to be very similar to that of dichlorotetrapyrazolenickel(II). The R value based upon 2104 observed reflections is 0.081.

Introduction

In dichlorotetrapyrazolenickel(II), Ni(Pz)₄Cl₂, the pyrazole (I) rings lie nearly parallel to the Ni-Cl direction



(Reimann, Mighell & Mauer, 1967) while in the related complex, dichlorotetrapyridinenickel(II), Ni(Py)₄Cl₂, the pyridine rings are inclined about 45° to the Ni-Cl direction (Porai-Koshits, 1954). In addition, the Ni-Cl distance is significantly longer in Ni(Pz)₄Cl₂ than in Ni(Py)₄Cl₂. Consequently the tetragonal distortion in the ligand field of the nickel ion is larger in the pyrazole complex than in the pyridine complex.

Dibromotetrapyridinenickel(II), Ni(Py)₄Br₂, has been investigated both structurally (Antsishkina & Porai-Koshits, 1958) and spectroscopically (Rowley & Drago,

1967). In view of the significant differences between the chloride complexes indicated above, dibromotetrapyrazolenickel(II), Ni(Pz)₄Br₂, was prepared so that it could be compared with the above compounds. Ni(Pz)₄Br₂ was found to have the same space group as Ni(Pz)₄Cl₂ with similar cell dimensions; this suggests that the gross structures are also similar. However, to compare these related complexes and to give a meaningful interpretation of their spectroscopic properties, it is necessary to determine bond distances and angles in the bromide complex. Therefore, the structure solution of Ni(Pz)₄Br₂ was undertaken.

Experimental and refinement

Crystals of Ni(Pz)₄Br₂ were grown from an aqueous solution of NiBr₂ and pyrazole. The crystal system and approximate cell parameters were determined from precession photographs taken with Cu $K\alpha$ radiation ($\lambda = 1.54051$ Å). The observed systematic absences are consistent with either Cc or $C2/c$. The centric space group was assigned on the basis of the complete structure determination. The 2θ angles of seventeen strong reflections in the range 20–45° were measured with a diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.710688$ Å), and the cell parameters were refined by least-squares analysis. The density was determined by flotation in a mixture of chloroform and ethylene dibromide. The crystal data are given in Table 1. For comparison, the cell dimensions of the related chloride complex, Ni(Pz)₄Cl₂, are also given.

Table 1. *Crystal data*

Ni(Pz) ₄ Br ₂	Ni(Pz) ₄ Cl ₂
$a = 14.127 (7) \text{ \AA}^*$	$a = 13.876 (1) \text{ \AA}$
$b = 9.334 (3)$	$b = 9.263 (6)$
$c = 14.702 (2)$	$c = 14.451 (3)$
$\beta = 118.62 (3)^\circ$	$\beta = 116.83 (1)^\circ$
Space group $C2/c$	Space group $C2/c$
$Z = 4$	$Z = 4$
$\rho_o = 1.94 \text{ g.cm}^{-3}\dagger$	$\rho_o = 1.61 \text{ g.cm}^{-3}$
$\rho_c = 1.92 \text{ g.cm}^{-3}$	$\rho_c = 1.61 \text{ g.cm}^{-3}$

* From least-squares refinement.

† From flotation in a mixture of chloroform and tetrabromoethane.

The intensities of 3079 unique reflections within $\sin \theta/\lambda = 0.756 \text{ \AA}^{-1}$ were measured with the peak height method. Of these, 2104 were considered as observed (for details relative to the collection of the data see Reimann, Mighell & Mauer, 1967). As the crystal used for the intensity measurements was a roughly spherical fragment with a diameter of 0.3 mm ($\mu_r = 1.0$), the absorption correction for spheres (*International Tables for X-ray Crystallography*, 1959) was applied.

The Ni and Br atomic coordinates were determined from a three-dimensional Patterson map which was calculated using the complete set of data. The atoms in the two crystal-

lographically independent pyrazole rings were located in an electron density map with phases calculated from the coordinate of the bromine and nickel atoms. This model was refined by full-matrix anisotropic least-squares analysis using all the data with the weighting scheme: $w = 1$ for $F_o < 50$ and $W = 50/F_o$ for $F_o > 50$. The refinement was carried out using scattering factors for neutral nickel, carbon, nitrogen, hydrogen and for singly negative bromine atoms taken from *International Tables for X-ray Crystallography* (1962). The hydrogen atoms in the pyrazole rings were then included in the calculations assuming that (i) the hydrogen atoms lie in the plane of the pyrazole rings, (ii) each hydrogen atom is equidistant from the two atoms adjacent to the atom to which the hydrogen is bonded and (iii) the C-H and N-H distances are 1 Å and 0.9 Å, respectively. An isotropic temperature factor ($B = 4.0$) was assigned to these hydrogen atoms. Final refinement on all atoms except hydrogen gave an agreement factor $R = 0.081$ based on 2104 observed reflections. A difference map ($F_o - F_c$) confirmed that the refined model was complete.

Comparison between the structures of Ni(Pz)₄Br₂ and of Ni(Pz)₄Cl₂ showed that they are very similar. For this reason they have been described in the same reference system with identical atom labelling. Therefore the atomic coordinates and the thermal parameters listed in Tables 2 and 3 are directly comparable with those of Ni(Pz)₄Cl₂. Structure factors are listed in Table 4.

Table 2. *Atomic coordinates**

	X/a	Y/b	Z/c
Ni	0	0	0
Br	0.08205 (5)	-0.18294 (7)	-0.08473 (5)
Ring 1			
N(1)	0.14517 (39)	-0.00952 (50)	0.14026 (36)
N(2)	0.16627 (54)	0.05607 (72)	0.22889 (46)
C(1)	0.26750 (71)	0.02721 (95)	0.30643 (58)
C(2)	0.31047 (65)	-0.06231 (98)	0.26323 (71)
C(3)	0.23353 (49)	-0.08307 (68)	0.16104 (50)
Ring 2			
N(3)	0.05685 (43)	0.17287 (50)	-0.04917 (39)
N(4)	0.10986 (68)	0.15524 (67)	-0.10410 (65)
C(4)	0.13699 (92)	0.28123 (92)	-0.12916 (89)
C(5)	0.09746 (73)	0.38529 (81)	-0.09341 (68)
C(6)	0.04761 (66)	0.31281 (66)	-0.04478 (61)

* The numbers in parentheses are standard deviations from least-squares in the last significant figures.

Table 3. *Anisotropic thermal parameters*

	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
Ni	415 (6)	514 (9)	306 (5)	-18 (6)	173 (4)	23 (5)
Br	648 (5)	736 (7)	504 (4)	55 (4)	330 (3)	-27 (4)
N(1)	458 (27)	637 (45)	333 (23)	30 (29)	161 (21)	57 (26)
N(2)	719 (44)	1103 (76)	438 (32)	-19 (47)	242 (31)	-71 (40)
C(1)	846 (60)	1295 (101)	440 (38)	-121 (63)	175 (40)	73 (50)
C(2)	585 (48)	1248 (103)	747 (57)	77 (56)	83 (43)	282 (63)
C(3)	465 (35)	795 (62)	484 (35)	68 (37)	195 (29)	45 (37)
N(3)	556 (32)	593 (45)	414 (26)	-24 (31)	255 (25)	65 (28)
N(4)	1147 (65)	810 (68)	992 (58)	-3 (51)	850 (56)	76 (48)
C(4)	1320 (89)	944 (82)	1166 (82)	12 (72)	950 (77)	165 (70)
C(5)	982 (67)	836 (83)	791 (57)	-105 (58)	526 (53)	194 (53)
C(6)	852 (55)	627 (59)	688 (46)	-104 (46)	497 (44)	-29 (43)

The numbers in parentheses are standard deviations in the last significant figures.

Table 4. Observed and calculated structure factors (x 10)

The columns are h, l, F0 and Fc, respectively. Reflections for which the net number of counts observed did not exceed zero by at least twice the standard deviation are marked by an L. The value assigned to the observed intensity for these reflections is equal to one standard deviation.

Table with multiple columns containing numerical data for structure factors. The table is organized into several sections, with some rows starting with 'h l' and others with 'F0 Fc'. The data includes various integers and some values marked with 'L'.

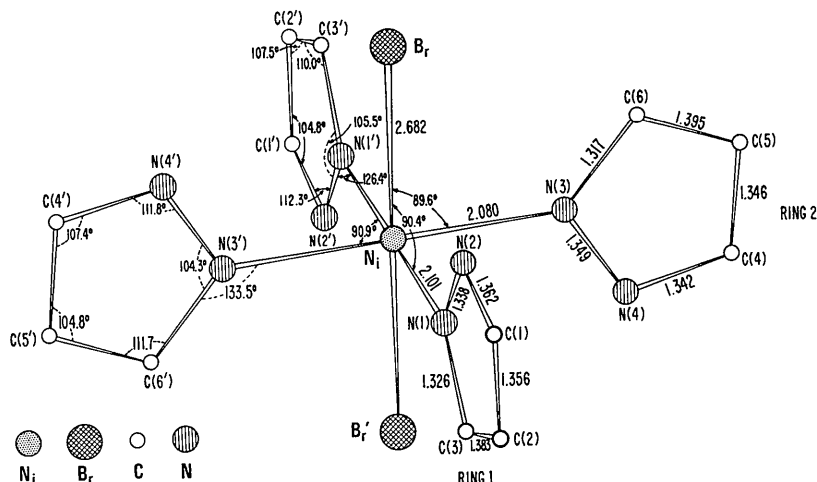


Fig. 1. Molecular structure of $\text{Ni}(\text{C}_3\text{H}_4\text{N}_2)_4\text{Br}_2$. Unique bond distances (Å) and angles are indicated.

$\text{Ni}(\text{Pz})_4\text{Cl}_2$. In the present case, ring 1 and ring 2 make angles of 91.2° and 91.8° respectively with the basal plane compared with 91.6° and 94.8° for the corresponding rings in $\text{Ni}(\text{Pz})_4\text{Cl}_2$. This orientation differs greatly from that observed in the analogous pyridine complexes in which the pyridine rings are inclined about 45° to the basal plane. The principal factor in this difference is undoubtedly the stabilization of the vertical orientation of the pyrazole rings by internal $\text{N}-\text{H}\cdots\text{X}$ hydrogen bonds. Fig. 1 shows that the hydrogen atoms bonded to N(4) and N(2) are suitably positioned for internal hydrogen bonding with the halogen atoms. Moreover, the existence of such hydrogen bonds can be inferred from the $\text{N}-\text{Cl}$ distances of 3.17 \AA for $\text{Cl}-\text{N}(2)$ and 3.10 \AA for $\text{Cl}-\text{N}(4)$ in $\text{Ni}(\text{Pz})_4\text{Cl}_2$ and the $\text{N}-\text{Br}$ distances of 3.33 \AA for $\text{Br}-\text{N}(2)$ and 3.21 \AA for $\text{Br}-\text{N}(4)$ in $\text{Ni}(\text{Pz})_4\text{Br}_2$. The influence of the internal hydrogen bonds is reflected in the greater length of the $\text{Ni}-\text{Cl}$ (2.507 \AA) and $\text{Ni}-\text{Br}$ (2.682 \AA) distances in the pyrazole complexes compared with the corresponding bonds in the pyridine complexes (2.38 \AA) and (2.58 \AA) (Antsishkina & Porai-Koshits, 1958). Thus it appears that in the pyridine compounds the orientation of the pyridine rings results from a compromise between the mutual repulsion of the pyridine rings and the repulsion between the rings and the halogen atoms, while in the pyrazole complexes the interaction between the halogen atoms and the pyrazole rings is a net attraction which stabilizes the vertical orientation.

The pyrazole rings were found by least squares to be planar to within experimental error. In Table 5 the ring bond distances reported here are compared with those determined in the chloride compound. A comparison shows that the closest similarity is achieved when crystallographically equivalent rings in the two different structures are compared. In particular, the bond between the non-coordinating nitrogen atom and the adjacent carbon atom is significantly longer in ring 1 than in ring 2 in both compounds. This consistency suggests that the differences in the $\text{N}-\text{C}$ bond lengths are real and they are probably due to the fact that ring 1 and ring 2 lie in different crystallographic environments.

All computer calculations on this structure were performed using the *Program System for X-ray Crystallography* (1967) developed at the University of Maryland in collabora-

Table 5. Comparison of bond distances between $\text{Ni}(\text{Pz})_4\text{Cl}_2$ and $\text{Ni}(\text{Pz})_4\text{Br}_2$

Bond	$\text{Ni}(\text{Pz})_4\text{Br}_2$	$\text{Ni}(\text{Pz})_4\text{Cl}_2$
Ni-Br(Cl)	2.682 (1) Å*	2.507 (1) Å
Ni-N(1)	2.101 (4)	2.097 (2)
Ni-N(3)	2.080 (5)	2.087 (3)
Ring 1		
N(1)-N(2)	1.338 (9)	1.345 (4)
N(2)-C(1)	1.362 (9)	1.357 (4)
C(1)-C(2)	1.356 (15)	1.371 (7)
C(2)-C(3)	1.383 (10)	1.393 (5)
C(3)-N(1)	1.326 (9)	1.329 (4)
Ring 2		
N(3)-N(4)	1.349 (14)	1.342 (6)
N(4)-C(4)	1.342 (13)	1.333 (6)
C(4)-C(5)	1.346 (16)	1.356 (6)
C(5)-C(6)	1.395 (15)	1.389 (6)
C(6)-N(3)	1.317 (8)	1.321 (4)

* The numbers in parentheses after the bond distances are standard deviations in the last significant figures.

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