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The Crystal and Molecular Structure of Hexapyrazolenickel(II) Nitrate, $\text{Ni}(\text{C}_3\text{H}_4\text{N}_2)_6(\text{NO}_3)_2$

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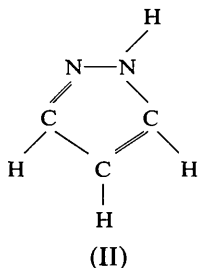
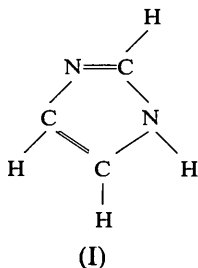
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The crystal structure of hexapyrazolenickel(II)nitrate, $\text{Ni}(\text{C}_3\text{H}_4\text{N}_2)_6(\text{NO}_3)_2$, was determined by single-crystal diffraction techniques. Crystals of $\text{Ni}(\text{C}_3\text{H}_4\text{N}_2)_6(\text{NO}_3)_2$ are trigonal with $a = 9.958$, $c = 7.278$ Å, space group $P\bar{3}$, $Z = 1$, $\rho_o = 1.57$, $\rho_c = 1.57$ g.cm⁻³. Three-dimensional counter data were collected (1115 reflections) and the structure was solved by an analysis of the Patterson map. The complex cation, $\text{Ni}(\text{C}_3\text{H}_4\text{N}_2)_6^{2+}$, formed by the coordination of six planar pyrazole molecules to the nickel ion, has $\bar{3}$ point symmetry. The nickel ion lies at the center of a nearly regular octahedron of coordinated nitrogen atoms. These complex cations and nitrate anions are linked by hydrogen bonds between each pyrrole type nitrogen atom ($\triangleright\text{N-H}$) in the pyrazole ring and an oxygen atom in the nitrate group. The final refinement by full-matrix anisotropic least-squares analysis resulted in an R value of 0.053.

Introduction

Five membered ring molecules which contain more than one nitrogen atom form a variety of complexes with transition metal ions. In these complexes important structural details depend upon the type and relative location of the nitrogen atoms. In each of several structures studied in this laboratory, the pyridine type nitrogen atoms ($\triangleright\text{N}$) are coordinated to a transition metal ion, and the pyrrole type nitrogen atoms ($\triangleright\text{N-H}$) participate in hydrogen bonding. The influence of the relative location of the nitrogen atoms in the ligand molecule on the structure of the complex is illustrated by some features of imidazole (I) and pyrazole (II) complexes



In hexaimidazolenickel(II)nitrate, $\text{Ni}(\text{Im})_6(\text{NO}_3)_2$ (Santoro, Mighell, Zocchi & Reimann, 1969), the coordinate bond and the N-H direction make an angle of $\sim 144^\circ$. In this complex the N-H groups form hydrogen bonds with oxygen atoms in NO_3^- groups located above and below neighboring $\text{Ni}(\text{Im})_6^{2+}$ cations. In dichlorotetrapyrazolenickel(II), $\text{Ni}(\text{Pz})_4\text{Cl}_2$ (Reimann, Mighell & Mauer, 1967) and dibromotetrapyrazolenickel(II), $\text{Ni}(\text{Pz})_4\text{Br}_2$ (Mighell, Reimann & Santoro, 1969) in which the coordinate bond and the N-H direction make an angle of $\sim 72^\circ$, the N-H group points toward the coordinated halogen atom to form an internal hydrogen bond.

Another pyrazole complex compound hexapyrazolenickel(II)nitrate, $\text{Ni}(\text{Pz})_6(\text{NO}_3)_2$, was prepared to compare its structural and spectroscopic properties with those of related complexes. The visible spectrum of $\text{Ni}(\text{Pz})_6(\text{NO}_3)_2$ was found to be almost identical with that of the related imidazole complex, $\text{Ni}(\text{Im})_6(\text{NO}_3)_2$. This indicates that the coordination about the nickel ion in these complexes is similar. However, the decrease from ~ 144 to $\sim 72^\circ$ in the angle between the coordinate bond and N-H direction would rule out a network of hydrogen bonds similar to that found in the imidazole complex. Moreover, internal hydrogen

bonding as found in $\text{Ni}(\text{Pz})_4\text{Cl}_2$ and $\text{Ni}(\text{Pz})_4\text{Br}_2$ cannot occur in $\text{Ni}(\text{Pz})_6(\text{NO}_3)_2$. Therefore, the solution of the structure of $\text{Ni}(\text{Pz})_6(\text{NO}_3)_2$ was undertaken to determine the structural changes associated with the different location of the N-H group in the coordinating molecule.

Experimental

Crystals of $\text{Ni}(\text{Pz})_6(\text{NO}_3)_2$ were grown by evaporation of a stoichiometric aqueous solution of $\text{Ni}(\text{NO}_3)_2$ and pyrazole. Crystal symmetry and approximate cell parameters were determined from zero and upper level precession photographs. The crystal belongs to the $\bar{3}$ Laue group with no classes of reflections systematically absent. Therefore the space group must be either $P\bar{3}$ or $P\bar{3}$. The centric space group ($P\bar{3}$) was assigned on the basis of the complete structure determination.

To determine precise unit-cell parameters, the 2θ angles of a set of reflections were measured on a single-crystal diffractometer using molybdenum radiation ($\lambda = 0.710688 \text{ \AA}$). The approximate cell parameters determined from the films were then refined by least-squares analysis to obtain the best agreement between the calculated and observed 2θ angles. Assuming $Z = 1$, the X-ray density was found to be 1.57 g.cm^{-3} . This value agrees with the density of 1.57 g.cm^{-3} measured by the flotation method. A summary of the crystal data is given in Table 1.

Table 1. *Crystal data for* $\text{Ni}(\text{NO}_3)_2(\text{C}_3\text{H}_4\text{N}_2)_6$

$a = 9.958 (2) \text{ \AA}$	Space group = $P\bar{3}$ (No. 147)
$c = 7.278 (2)$	$Z = 1$
$\rho_o = 1.57 \text{ g.cm}^{-3}$	$\rho_c = 1.57 \text{ g.cm}^{-3}$

A ditrigonal prismatic crystal was mounted on a single-crystal diffractometer with the c axis parallel to the ϕ axis of the goniometer. Intensities were recorded by the scan method for all reflections having 2θ up to 42° and by the stationary-counter stationary-crystal method for reflections with 2θ between 42 and 58° . Mo $K\alpha$ radiation was used for measuring the intensities. Background intensities were determined at $2\theta \pm \frac{1}{2}\Delta 2\theta$ where $\Delta 2\theta = 1.9 + 1.0 \tan \theta$. For the peak-height intensities, the counting time was 10 seconds on the peak and on each background; for the scan intensities, the rate of scanning was 2° min^{-1} , and the background counting times were 10 seconds. Reflections for which the net number of counts observed did not exceed zero by at least twice the standard deviation were tagged as 'less thans' and assigned the net number of counts equal to one standard deviation. To convert the observed peak height intensities (I_o) to integrated intensities (I_i), strong reflections spanning the measured 2θ range were also determined by the scan method. A curve of I_i/I_o versus 2θ was utilized to obtain the conversion of the peak height data to integrated intensity

data. A total of 1115 reflections were measured of which 273 were labeled as 'less thans'.

The intensity data were corrected for Lorentz and polarization factors. No absorption correction was applied because the linear absorption coefficient of this compound is small (8.6 cm^{-1} for Mo $K\alpha$) and the minimum and maximum dimensions of the crystal used were about 0.2 and 0.3 mm respectively. (A sphere having the same linear absorption coefficient and a diameter equal to the maximum dimension of the prism (0.3 mm) would have a $\mu R = 0.1$.)

Determination and refinement

As indicated in Table 1, the unit cell contains one molecule of $\text{Ni}(\text{Pz})_6(\text{NO}_3)_2$. In the centrosymmetric space group $P\bar{3}$, the sites of the nickel atoms must have symmetry $\bar{3}$ and those of the nitrate nitrogen atoms symmetry 3. Thus the structure is specified completely by the coordinates of the atoms in one pyrazole ring, by the z coordinate of the nitrate nitrogen atom and by the coordinates of one oxygen atom.

To determine the structure, a three-dimensional Patterson map was calculated using the complete set of observed data. A set of five peaks near the origin was identified as the pyrazole ring atoms by the spatial relationships between them. The atom closest to the origin was labeled as a nitrogen atom. The other nitrogen atom in the ring was tentatively assigned on the basis of peak size. An electron-density map, calculated with phases determined by the nickel atom and the pyrazole ring atoms revealed the nitrate anion about the special position with symmetry 3 located at $\frac{1}{3}, \frac{2}{3}, z$.

The trial model was refined by full-matrix least-squares analysis. The quantity minimized was $\sum w(F_o - F_c)^2$ with the weighting scheme $w = 1$ for $F_o < 22$ and $w = 22/F_o$ for $F_o > 22$. Reflections assigned as 'less thans' received zero weight unless the value of F_c exceeded the value of F_o . When this occurred the reflections were assigned unit weight. The scattering factors used in the calculations are those given in *International Tables for X-ray Crystallography* (1962) for neutral nickel, nitrogen, carbon and hydrogen atoms and for the (O^-) oxygen atom. After three cycles of isotropic refinement, the R value ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) based on 842 observed reflections was 0.12. To verify the assignment of the non-coordinating nitrogen atom, the structure was refined with N(2) and C(3) interchanged. The significant increase in the R value (~ 0.01) which resulted corroborates the initial assignment. The ring hydrogen atoms were then introduced into the calculations assuming that: (i) the hydrogen atoms lie in the plane of the pyrazole ring, (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 0.95 and 0.87 \AA respectively. This model was then refined with 3 cycles of full-matrix anisotropic least-squares analysis to an R value of 0.053. In this refinement the hydrogen

Table 2. Atomic coordinates for hexapyrazolenickel(II) nitrate

	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>
Ni	0	0	0
C(1)	0.65145 (42)*	0.59487 (40)	0.27699 (59)
C(2)	0.77712 (46)	0.60165 (43)	0.35901 (57)
C(3)	0.90375 (41)	0.73175 (42)	0.28738 (55)
N(1)	0.86050 (28)	0.80305 (29)	0.16620 (42)
N(2)	0.70390 (30)	0.71612 (30)	0.16146 (44)
N(3)	$\frac{1}{3}$	$\frac{2}{3}$	0.12200 (81)
O(1)	0.21091 (34)	0.67160 (35)	0.11909 (60)

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

atom parameters were held constant. Finally a difference Fourier synthesis was calculated and no spurious peaks were observed. The final atomic coordinates, the anisotropic thermal parameters, and the structure factors are reported in Tables 2, 3, and 4.

Description and discussion

The crystal structure of Ni(Pz)₆(NO₃)₂ viewed along the *c* axis is shown in Fig. 1. The nickel ion occupies the $(\bar{3})$ special position at (0,0,0) and the nitrate nitrogen atoms lie on the (3) special positions at $(\frac{2}{3}, \frac{1}{3}, z$:

Table 3. Anisotropic thermal parameters

The general anisotropic temperature factor has the form

$$\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})].$$

	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
Ni	772 (13)	772 (13)	2159 (24)	386 (7)	0	0
C(1)	1239 (50)	1020 (44)	3115 (100)	350 (40)	269 (56)	239 (53)
C(2)	1569 (58)	1315 (52)	2850 (97)	697 (46)	344 (60)	475 (57)
C(3)	1246 (48)	1327 (50)	2838 (94)	709 (42)	70 (52)	234 (54)
N(1)	832 (32)	917 (34)	2416 (64)	383 (28)	77 (36)	98 (37)
N(2)	869 (34)	891 (34)	2772 (73)	351 (28)	-26 (38)	23 (39)
N(3)	1159 (62)	1159 (62)	2767 (123)	580 (31)	0	0
O(1)	1357 (43)	1615 (48)	6517 (139)	832 (38)	-129 (61)	24 (63)

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

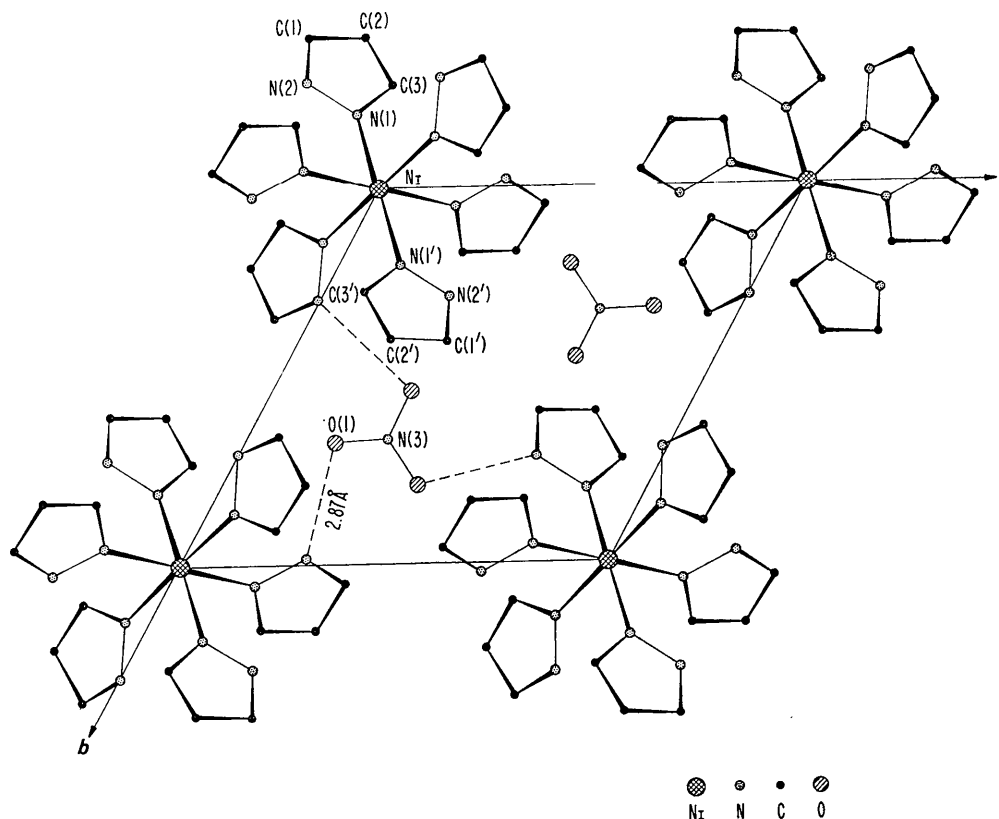


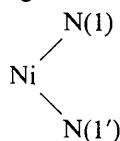
Fig. 1. Crystal structure of hexapyrazolenickel(II) nitrate, Ni(Pz)₆(NO₃)₂, projected along the *c* axis. The shortest cation-anion (distance indicated by dotted lines in the Figure) is between N(2) of the cation and O(1) of the nitrate anion. The N(3)-O(1) bond distance in the nitrate anion is 1.245 (4) Å.

Table 4. Observed and calculated structure factors ($\times 10$)

L = 0		L = 1		L = 2		L = 3		L = 4		L = 5		L = 6		L = 7	
1	0	378	368	2	5	216	213	-2	4	94	90	6	4	38	28
1	0	189	184	3	5	148	144	-3	4	321	327	6	4	99	99
1	0	126	122	4	5	108	104	-4	4	271	277	6	4	66	66
1	0	90	88	5	5	72	70	-5	4	196	192	6	4	45	45
1	0	54	52	6	5	48	46	-6	4	146	142	6	4	30	30
1	0	36	34	7	5	36	34	-7	4	106	102	6	4	20	20
1	0	24	22	8	5	24	22	-8	4	76	72	6	4	14	14
1	0	18	16	9	5	18	16	-9	4	56	52	6	4	10	10
1	0	12	10	10	5	12	10	-10	4	40	36	6	4	7	7
1	0	9	8	11	5	9	8	-11	4	30	26	6	4	5	5
1	0	6	5	12	5	6	5	-12	4	22	18	6	4	4	4
1	0	4	3	13	5	4	3	-13	4	16	12	6	4	3	3
1	0	3	2	14	5	3	2	-14	4	12	8	6	4	2	2
1	0	2	1	15	5	2	1	-15	4	8	6	6	4	1	1
1	0	1	0	16	5	1	0	-16	4	6	4	6	4	0	0
1	0	0	0	17	5	0	0	-17	4	4	3	6	4	0	0
1	0	0	0	18	5	0	0	-18	4	3	2	6	4	0	0
1	0	0	0	19	5	0	0	-19	4	2	1	6	4	0	0
1	0	0	0	20	5	0	0	-20	4	1	0	6	4	0	0
1	0	0	0	21	5	0	0	-21	4	0	0	6	4	0	0
1	0	0	0	22	5	0	0	-22	4	0	0	6	4	0	0
1	0	0	0	23	5	0	0	-23	4	0	0	6	4	0	0
1	0	0	0	24	5	0	0	-24	4	0	0	6	4	0	0
1	0	0	0	25	5	0	0	-25	4	0	0	6	4	0	0
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1	0	0	0	28	5	0	0	-28	4	0	0	6	4	0	0
1	0	0	0	29	5	0	0	-29	4	0	0	6	4	0	0
1	0	0	0	30	5	0	0	-30	4	0	0	6	4	0	0
1	0	0	0	31	5	0	0	-31	4	0	0	6	4	0	0
1	0	0	0	32	5	0	0	-32	4	0	0	6	4	0	0
1	0	0	0	33	5	0	0	-33	4	0	0	6	4	0	0
1	0	0	0	34	5	0	0	-34	4	0	0	6	4	0	0
1	0	0	0	35	5	0	0	-35	4	0	0	6	4	0	0
1	0	0	0	36	5	0	0	-36	4	0	0	6	4	0	0
1	0	0	0	37	5	0	0	-37	4	0	0	6	4	0	0
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1	0	0	0	47	5	0	0	-47	4	0	0	6	4	0	0
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1	0	0	0	112	5	0	0	-112	4	0	0	6	4	0	0
1	0	0	0	113	5	0	0	-113	4	0	0	6	4	0	0
1	0	0	0	114	5	0	0	-114	4	0					

$\frac{1}{3}, \frac{2}{3}, \bar{z}$). In this configuration, each pyrazole molecule utilizes the pyridine type nitrogen atom in coordination and the N-H group in hydrogen bonding.

The structure of the $\text{Ni}(\text{Pz})_6^{2+}$ cation, including all unique bond distances and angles, is shown in Fig. 2. The pyrazole ligand was found by least-squares analysis to be planar to within experimental error. Bond distances and angles, including their standard deviation, for coordinated pyrazole are given in Table 5. The nickel ion is virtually coplanar with each pair of centrosymmetrically related pyrazole molecules as it lies only 0.1 Å from the extended plane of each ring. The coordination polyhedron about the nickel ion is very nearly a regular octahedron. The actual configuration of the six coordinating nitrogen atoms may be described as resulting from a compression of 0.02 Å along one of the threefold axes of a regular octahedron. The compression (along the c axis) is reflected in a



angle of 89.2° (see Fig. 2).

Table 5. Bond distances and angles for the pyrazole ligand in $\text{Ni}(\text{Pz})_6(\text{NO}_3)_2$

N(1)-N(2)	1.354 (3)* Å		$104.6 (3)^\circ$
N(2)-C(1)	1.344 (5)		$111.4 (3)$
C(1)-C(2)	1.357 (7)		$107.2 (3)$
C(2)-C(3)	1.381 (5)		$105.5 (4)$
C(3)-N(1)	1.332 (6)		$111.3 (4)$

* The numbers in parentheses are the standard deviation in the last significant figure. These standard deviations are from the final cycle of least-squares requirement.

A comparison of the structures of the pyrazole and imidazole complexes, $\text{Ni}(\text{Pz})_6(\text{NO}_3)_2$ and $\text{Ni}(\text{Im})_6(\text{NO}_3)_2$, (Santoro *et al.*, 1969) shows that in both cases the coordination is octahedral, that the complex cation has symmetry $\bar{3}$, and that the NO_3^-

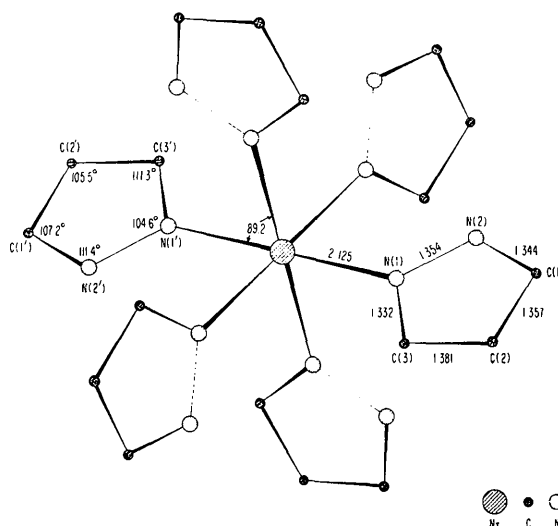


Fig. 2. The complex cation, $\text{Ni}(\text{Pz})_6^{2+}$. The unique bond distances and angles are indicated. The coordination octahedron is specified by the Ni-N(1) coordinate distance of 2.125 (3) Å and the unique angle of 89.2° .

group has symmetry 3. These two structures, however, differ in molecular packing. Specifically, they differ in the utilization of threefold special positions. In $\text{Ni}(\text{Pz})_6(\text{NO}_3)_2$ (space group $P\bar{3}$), the $\text{Ni}(\text{Pz})_6^{2+}$ cation and the nitrate anions are located on different threefold axes; in $\text{Ni}(\text{Im})_6(\text{NO}_3)_2$ (space group $R\bar{3}$), the $\text{Ni}(\text{Im})_6^{2+}$ cation and nitrate anions are located on the same threefold axes. In both complexes the (-N-H) groups have the proper orientation relative to the nearest NO_3^- groups to form hydrogen bonds.

To accommodate hydrogen bonding, there is considerable variation in the position of the ligand rings relative to each other in these complexes. For example, in $\text{Ni}(\text{Pz})_6^{2+}$ the normal to each pyrazole ligand makes an angle of 42.9° with the c axis, whereas in $\text{Ni}(\text{Im})_6^{2+}$ this angle is 65.5° . This difference notwithstanding, both the coordinate bond lengths and angles in the coordination polyhedra in these two structures are nearly identical. As the visible spectra depend upon the ligand field about the metal ion, the near identity of the coordination polyhedra in $\text{Ni}(\text{Pz})_6(\text{NO}_3)_2$ and $\text{Ni}(\text{Im})_6(\text{NO}_3)_2$ accounts for the marked similarity in their spectra.

Three structures involving pyrazole coordinated to nickel(II) are now available for comparison: $\text{Ni}(\text{Pz})_6(\text{NO}_3)_2$, $\text{Ni}(\text{Pz})_4\text{Cl}_2$, $\text{Ni}(\text{Pz})_4\text{Br}_2$. In the chloride and bromide complexes there are two sets of crystallographically independent pyrazole rings which gives a total of five independent sets of ring parameters in the three structures. In all cases the pyrazole ring is planar, and the range of ring bond distances is relatively narrow. In each ring, the shortest bond distance corresponds to the classical double bond between N(1) and C(1) and the longest corresponding to the classical single bond between C(1) and C(2).

This feature is also present in the calculated bond distances for pyrazole (Dewar & Gleicher, 1966).

The planarity of the pyrazole rings and the narrow range of bond distances indicate that resonance is important in the description of the pyrazole molecule. The proximity of the nickel ion may be expected to reduce the electron density in the rings which would decrease the resonance and act to restore the single and double bond distances toward their classical values. If this is the case, a variable coordinate bond distance may be accompanied by measurable changes in the ring bond distances. In the structure of the three pyrazole complexes, the distances from the nickel ion to the coordinated nitrogen atom have five different values from 2.080 to 2.125 Å. A sensitive indicator of a change in resonance would be the difference (Δ) be-

tween the longest [C(1)–C(2)] and shortest [N(1)–C(1)] bond lengths. In Table 6 this difference (Δ) is given along with the corresponding Ni···N coordinate distance. The values in the Table show that although the differences are small there is a trend in the expected direction; *i.e.* Δ decreases with increasing coordination distance. It should be pointed out that the calculated bond distances for non-coordinated pyrazole (Dewar & Gleicher, 1966) have a $\Delta=0.16$ which is greater than that observed in any of the five coordinated pyrazole molecules discussed here. This suggests that the resonance contribution to the structure of non-coordinated pyrazole may have been underestimated in the theoretical calculations.

All computer calculations on this structure were performed using the *Program System for X-ray Crystallography* (1967) developed at the University of Maryland in collaboration with the National Bureau of Standards and the Geological Survey. The authors would like to thank Floyd Mauer of NBS and Professor P. Willis of Hood College for their assistance in the collection and processing of the diffraction data.

Table 6. Correlation between the Ni···N coordinate bond distance and (Δ) in three pyrazole complexes

Δ is defined as the difference between the shortest ring bond distance [N(1)–C(1)] and the longest ring bond distance [C(1)–C(2)].

Coordinate bond distance

[Ni···N]	$\Delta = \{[C(1)–C(2)] - [N(1)–C(1)]\}$
2.125 Å*	0.049 Å
2.101†	0.057
2.097‡	0.064
2.087 ‡	0.068
2.080†	0.078

* Hexapyrazolenickel(II) nitrate, Ni(Pz)₆(NO₃)₂ (this paper). In this compound there is one crystallographically independent pyrazole ring.

† Dibromotetrapyrazolenickel(II), Ni(Pz)₄Br₂. (Mighell *et al.*, 1969). In this compound there are two crystallographically independent pyrazole rings.

‡ Dichlorotetrapyrazolenickel(II), Ni(Pz)₄Cl₂. (Reimann *et al.*, 1967). In this compound there are two crystallographically independent pyrazole rings.

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The Crystal Structure of the 1:4 Calcium Bromide–Diacetamide Complex

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The crystal structure of CaBr₂·4C₄H₇NO₂ has been determined by three-dimensional X-ray methods. Data were collected by automatic counting methods and agreement of $R=0.08$ was obtained after full-matrix anisotropic refinement. Each calcium ion was found to be chelated by four molecules of diacetamide and to lie at the centre of an antiprism defined by the eight oxygen ligands. The bromide ions do not occur in the calcium coordination spheres, but lie halfway between nitrogen atoms within layers of diacetamide molecules parallel to (001).

Introduction

According to the mechanism proposed for the complexing of alkali metal halides with diacetamide (Roux

& Boeyens, 1969*b*) one would expect alkaline earth metal halides to form 1:2 complexes in which the metal ion lies centrally in the plane of four oxygen ligands and with two halide ions completing a coordination octahedron around it. These salts, however, invariably form 1:4 complexes (Gentile & Shankoff, 1965) and their geometries can thus be expected to be of a differ-

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