multiple bonding in that linkage of the cage molecule. It seems likely that the $p\pi-d\pi$ bonding between nitrogen and phosphorus which is usually discussed is not allowed on a symmetry basis because of the constraints imposed in forming the cage framework. The $(p \rightarrow d)\pi$ overlap would involve the same geometric arguments invoked by Cruickshank for tetrahedral oxyanions.[15] With this approach the two best p–d overlaps possible for pyramidal geometry would both require the p orbitals to be canted with respect to the plane of the three donating atoms, which is not possible in $P_2(NCH_3)_6$ because of its bicyclic structure.

Acknowledgments.—The authors wish to acknowledge the support of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation's Program of College Teacher Research Participation. We are also grateful to the University of Arkansas for providing computer facilities for this work.

[15] D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SECTION OF INORGANIC CHEMISTRY AND SECTION OF X-RAY AND ELECTRON DIFFRACTION, STATE UNIVERSITY, LEIDEN, THE NETHERLANDS

Pyrazoles and Imidazoles as Ligands. XIV.[1] The Crystal and Molecular Structure of Dibromotetrakis(5-methylpyrazole)manganese(II), $Mn(C_4H_6N_2)_4Br_2$

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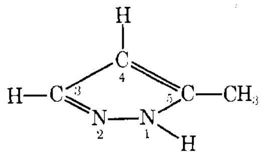
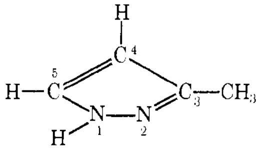
The crystal and molecular structure of dibromotetrakis(5-methylpyrazole)manganese(II), $Mn(C_4H_6N_2)_4Br_2$, has been determined by single-crystal X-ray diffraction techniques. The compound crystallizes in the triclinic system, space group $P\bar{1}$, with a = 8.802 (6) Å, b = 9.695 (5) Å, c = 7.613 (8) Å, α = 105.12 (4)°, β = 114.98 (4)°, γ = 92.90 (3)°, and Z = 1. Data to $(\sin\theta)/\lambda = 0.77$ (Mo Kα radiation) were collected with a three-circle diffractometer, and the structure was solved and refined by conventional heavy-atom techniques and least-squares refinement. The final least-squares cycle gave a conventional R factor of 0.045 for those 2590 reflections above the background. The compound consists of discrete units *trans*-$Mn(C_4H_6N_2)_4Br_2$, crystal symmetry $C_i(\bar{1})$, separated by normal van der Waals distances. The coordination polyhedron around the Mn(II) ion has approximately D_{4h} symmetry and is built up by four nitrogens of the 5-methylpyrazole ligands and two bromine anions.

Introduction

Previous work from this laboratory dealt with synthesis,[2] ligand-field spectra,[3] vibrational spectra,[4] and epr spectra[5] of coordination compounds containing the ligand 3(5)-methylpyrazole (hereafter called mpz). In this ligand the methyl group may be located at either the 3 or the 5 position in the heterocyclic ring, due to the acidic character of the imino hydrogen.



5-methylpyrazole



3-methylpyrazole

Stereometric considerations, comparison with complexes of 4-methylpyrazole and 3,5-dimethylpyrazole, and vibrational spectra led to the conclusion that in coordination compounds mpz is present as 5-methylpyrazole rather than 3-methylpyrazole.[2] In addition epr measurements of the present compound[5] indicated a trans location of the bromine anions and an approximate symmetry of D_{4h}. To investigate the validity of these conclusions the crystal structure determination of $Mn(mpz)_4Br_2$ has been undertaken.

Unit Cell and Space Group

Crystals of $Mn(mpz)_4Br_2$ were grown as colorless needles from alcoholic solutions of $MnBr_2(H_2O)_3$ and the stoichiometric amount of mpz, as described previously.[2]

Crystal symmetry and approximate cell parameters were determined from zero and upper level Weissenberg photographs. The crystal belongs to the Laue group $\bar{1}$; therefore the space group must be either $P\bar{1}$ or $P1$. The consistency of the results justified the initially chosen space group $P\bar{1}$.

The precise unit cell parameters were determined on a single-crystal diffractometer at 20°, using Mo Kα radiation (λ 0.71069 Å). The parameters are a = 8.802 (6) Å, b = 9.695 (5) Å, c = 7.613 (8) Å, α = 105.12 (4)°, β = 114.98 (4)°, and γ = 92.90 (3)°, which were obtained from θ, φ, and χ measurements of 14 $h00$, $0k0$, and $00l$ reflections and refined by least-squares procedures. Estimated standard deviations in the least significant digits are in parentheses. The density measured by the flotation method in CCl_4-$CHCl_3$ of 1.600 (5) g/cm^3 agrees with a value of 1.593 g/cm^3 calculated for Z = 1 and a molecular weight of 543.

Collection and Reduction of X-Ray Diffraction Data

A crystal of approximate size 0.7 × 0.3 × 0.3 mm with well-developed (100) and (010) faces was mounted on an Enraf-Nonius three-circle single-crystal diffractometer, with the plane $(11\bar{2})$ perpendicular to the φ axis. Intensities were recorded by the θ–2θ scan method for all reflections with θ between 3 and 33°. Zr-filtered Mo Kα radiation was used for measuring the intensities. Background intensities were determined at $2\theta \pm {}^1/_2\Delta$, with $\Delta = 1.2 + 0.9 \tan\theta$. The mean counting time was 33 sec for each background and 66 sec for the scan.

By this method a total of 3879 reflections were measured, from which 2590 had intensities greater than twice the standard deviation (σ); these σ's were calculated from the statistical inaccuracy of the measurements, with an amount added for errors in the absorption correction and attenuation factors. All data

[1] Part XIII: J. Reedijk and J. A. Smit, *Recl. Trav. Chim. Pays-Bas*, **90**, 1135 (1971).

[2] J. Reedijk, *ibid.*, **89**, 605 (1970).

[3] J. Reedijk, *ibid.*, **89**, 993 (1970).

[4] J. Reedijk, *ibid.*, **90**, 117 (1971).

[5] R. D. Dowsing, B. Nieuwenhuyse, and J. Reedijk, *Inorg. Chim. Acta*, **5**, 301 (1971).

were corrected for Lorentz and polarization effects. At a later stage, when a computer program developed by Mr. R. A. G. de Graaff became available,[6] absorption corrections were also applied. Calculated transmission factors were between 0.51 and 0.61 ($\mu = 43.9\ \text{cm}^{-1}$).

After reduction of the intensities to F values a Wilson plot[7] was calculated from which were obtained approximate values for the scale factor and the initial overall isotropic thermal parameter B.

Solution and Refinement of the Structure

All crystallographic calculations were carried out using the Leiden University IBM 360/50 computer, with the aid of a set of computer programs written or modified by Mrs. E. W. Rutten-Keulemans and Mr. R. A. G. de Graaff.[6,8]

Scattering factors for neutral nitrogen and carbon were taken from ref 9; scattering factors for hydrogen were taken from Stewart, *et al.*[10] The manganese(II) and bromine(I−) scattering factors of Cromer and Waber[11] were used after correction for the real part of the anomalous dispersion, $\Delta f'$.

The function minimized during the least-squares refinement process was $\Sigma w(|F_o| - |F_c|)^2$, with the weighting scheme $w = 1/(\sigma_F)^2$. Discrepancy indices referred to are $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_{wF} = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

A first three-dimensional Patterson synthesis revealed the positions of manganese and bromine. Manganese was placed at the origin (0, 0, 0) and a minimum function with a shift over the Br–Br vector was calculated, yielding rough positions for all nitrogens and a few carbons. A difference Fourier synthesis phased by these atoms ($R_F = 0.25$) revealed the positions of all other nonhydrogen atoms. Four cycles of full-matrix refinement of positional parameters and individual isotropic thermal parameters for the 27 nonhydrogen atoms led to convergence at $R_F = 0.114$.

At this stage the absorption correction was applied to the diffraction data. Although a full-matrix calculation should be the best procedure, due to the limited computer storage a block-diagonal version of the least-squares program was used[8] from this stage. Three new cycles of least-squares refinement, applying anisotropic thermal parameters for Mn and Br, yielded $R_F = 0.062$ ($R_{wF} = 0.081$). Next, hydrogens were placed at calculated positions, *i.e.*, 1.00 Å from C or N, assuming sp^3 and sp^2 hybridization for the attached C and N, with isotropic thermal parameters of 4.0 Å^2. Two additional cycles of least-squares refinement of positional and individual anisotropic thermal parameters for all nonhydrogen atoms led to $R_F = 0.052$ ($R_{wF} = 0.062$).

A difference Fourier synthesis at this stage showed (i) small peaks (less than 1 e$^-$/Å^3) in the vicinity of Mn and Br, (ii) indications for more than one conformation of the methyl groups, and (iii) deviations from the calculated positions of the hydrogen atoms attached directly to the five-membered rings. Therefore in the next stage positional and isotropic thermal parameters of the hydrogen atoms were also refined, taking into account the two conformations of the CH_3 groups, each with 50% population. With the parameters blocked in 14 submatrices, three cycles of refinement in this way led to convergence at $R_F = 0.045$ ($R_{wF} = 0.050$).

Because of the fact that in the last cycle the parameter shifts were less than one-fifth of the estimated standard deviations the refinement was considered to be finished. A final difference Fourier synthesis had only some small peaks in the vicinity of Mn and Br; this may reflect the fact that the imaginary part of the dispersion correction was not included. Observed and calculated structure factors for all 3879 reflections are shown in Table I.[12] The final scale factor was 0.2662. Atomic parameters are collected in Tables II and III. The anisotropic thermal parameters for the nonhydrogen atoms are listed in Table IV.

TABLE II[a]

POSITIONAL PARAMETERS OF NONHYDROGEN ATOMS ($\times 10^4$)

Atom	x/a	y/b	z/c
Mn	0	0	0
Br	1680 (1)	673 (1)	4138 (1)
N(1)	−2199 (4)	905 (4)	317 (4)
N(2)	1071 (4)	2212 (4)	141 (4)
N(3)	−2307 (4)	1275 (4)	2097 (4)
N(4)	1033 (5)	2537 (4)	−1494 (5)
C(1)	1792 (6)	3449 (5)	1622 (6)
C(2)	−3568 (5)	1279 (4)	−949 (5)
C(3)	−4520 (5)	1873 (4)	17 (6)
C(4)	−3683 (4)	1853 (4)	1975 (5)
C(5)	−4033 (8)	2352 (7)	3752 (8)
C(6)	2179 (7)	4541 (5)	924 (6)
C(7)	1662 (5)	3917 (4)	−1089 (6)
C(8)	1748 (15)	4512 (7)	−2642 (11)

[a] Estimated standard deviations in the least significant digits are in parentheses for this and for following tables.

TABLE III

POSITIONAL PARAMETERS ($\times 10^3$) AND ISOTROPIC TEMPERATURE FACTORS (Å^2 × 10) FOR THE HYDROGEN ATOMS

Atom[a]	x/a	y/b	z/c	B
H(1)	199 (6)	345 (5)	276 (6)	62 (12)
H(2)	−374 (4)	116 (4)	−228 (5)	28 (6)
H(3)	−563 (5)	225 (4)	−60 (5)	39 (8)
H(6)	264 (6)	551 (5)	163 (6)	59 (11)
H(51)[b]	−401 (13)	339 (9)	397 (12)	40 (18)
H(52)	−340 (11)	229 (11)	504 (12)	30 (15)
H(53)	−517 (14)	182 (12)	339 (14)	52 (23)
H(54)[c]	−315 (12)	304 (11)	478 (15)	45 (21)
H(55)	−413 (12)	159 (9)	423 (12)	31 (16)
H(56)	−489 (15)	263 (13)	335 (13)	48 (23)
H(81)[b]	115 (10)	545 (8)	−249 (10)	31 (15)
H(82)	157 (11)	388 (7)	−378 (11)	19 (13)
H(83)	320 (10)	487 (10)	−179 (11)	32 (15)
H(84)[c]	97 (11)	427 (11)	−345 (15)	10 (21)
H(85)	265 (19)	381 (15)	−303 (23)	103 (40)
H(86)	232 (15)	527 (12)	−225 (14)	51 (23)
NH(3)[d]	−163 (4)	94 (3)	310 (5)	29 (7)
NH(4)	78 (5)	190 (4)	−252 (6)	43 (9)

[a] The first figure of the number in parentheses corresponds to the carbon atom to which the hydrogen is attached. [b] Two sets of hydrogens were used for C(5) and C(8) to allow for disorder; the first three hydrogens correspond to the first set. [c] These three hydrogens correspond to the second set of hydrogens. [d] NH means a proton attached to a nitrogen.

TABLE IV[a]

ANISOTROPIC TEMPERATURE FACTORS OF NONHYDROGEN ATOMS (Å^2 × 10^4)

Atom	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{31}$
Mn	390 (3)	503 (4)	414 (3)	211 (6)	379 (6)	444 (6)
Br	419 (2)	639 (2)	355 (1)	148 (3)	342 (3)	339 (3)
N(1)	411 (14)	542 (16)	400 (14)	240 (25)	312 (24)	414 (23)
N(2)	470 (15)	525 (16)	423 (14)	177 (26)	370 (25)	434 (25)
N(3)	412 (15)	577 (17)	372 (14)	296 (26)	325 (25)	370 (24)
N(4)	566 (18)	458 (16)	389 (15)	94 (27)	283 (26)	372 (27)
C(1)	888 (31)	590 (23)	462 (21)	300 (43)	318 (36)	703 (43)
C(2)	467 (18)	568 (20)	428 (17)	263 (31)	419 (31)	337 (30)
C(3)	443 (18)	566 (21)	581 (21)	371 (33)	435 (34)	430 (33)
C(4)	410 (17)	421 (17)	511 (18)	199 (27)	202 (28)	467 (29)
C(5)	690 (33)	774 (37)	626 (29)	509 (60)	336 (53)	808 (53)
C(6)	1099 (38)	458 (22)	557 (23)	131 (46)	206 (37)	770 (49)
C(7)	721 (25)	470 (19)	545 (20)	168 (36)	391 (32)	599 (38)
C(8)	1679 (96)	522 (35)	654 (39)	−101 (90)	386 (60)	1057 (108)

[a] The general anisotropic temperature factor has the form $\exp(-2\pi^2(\Sigma_i\Sigma_j U_{ij}h_ih_ja_i^*a_j^*))$.

The Molecular Structure

Intramolecular distances and their estimated standard deviations (esd's) are shown in Table V, whereas bond angles with esd's are given in Table VI.

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[6] R. A. G. de Graaff, to be submitted for publication.

[7] A. J. C. Wilson, *Nature (London)*, **150**, 152 (1942).

[8] H. J. Geise, C. Romers, and E. W. M. Rutten, *Acta Crystallogr.*, **20**, 249 (1966).

[9] J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, pp 210–212.

[10] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

[11] D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

[12] Table I, a listing of structure factor amplitudes, will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036 by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy and $2.00 for microfiche.

TABLE V[a]
INTRAMOLECULAR DISTANCES (Å) AND THEIR ESTIMATED STANDARD DEVIATIONS[b]

Mn–Br	2.727 (2)	C(4)–C(5)	1.478 (5)
Mn–N(1)	2.243 (3)	C(2)–H(2)	0.93 (3)
Mn–N(2)	2.256 (3)	C(3)–H(3)	1.02 (4)
Mn···N(3)	3.188 (3)	N(3)–NH(3)	0.90 (3)
Mn···N(4)	3.205 (3)	C(5)–H_{av}[c]	0.92 (10)
Mn···C(1)	3.296 (5)	Ring II	
Mn···C(2)	3.296 (4)	N(2)–N(4)	1.348 (4)
Br···N(3)	3.338 (4)	N(2)–C(1)	1.314 (5)
Br···N(4′)	3.370 (4)	C(1)–C(6)	1.389 (6)
Br···C(1)	3.708 (5)	C(6)–C(7)	1.349 (6)
Br···C(2′)	3.684 (4)	C(7)–N(4)	1.327 (5)
Ring I		C(7)–C(8)	1.471 (7)
N(1)–N(3)	1.354 (4)	C(1)–H(1)	0.81 (5)
N(1)–C(2)	1.325 (4)	C(6)–H(6)	0.92 (5)
C(2)–C(3)	1.387 (5)	N(4)–NH(4)	0.80 (4)
C(3)–C(4)	1.362 (6)	C(8)–H_{av}[c]	0.94 (12)
C(4)–N(3)	1.338 (4)		

[a] Atoms marked with a prime are related to atoms of the same number by an inversion center. [b] The esd's in distances and in angles (Table VI) include the esd's in the cell parameters. [c] All six C–H distances have been averaged; individual distances were found to range from 0.7 to 1.1 Å.

The stereochemistry of dibromotetrakis(5-methylpyrazole)manganese(II) and the system for labeling of the atoms are depicted in Figure 1. We observe that the methyl groups are unambiguously at the 5 position of the ring. This was suggested before[2] from stereometric considerations and physical measurements.[3–5]

TABLE VI
BOND ANGLES AND THEIR ESTIMATED STANDARD DEVIATIONS[a]

Atoms	Angles, deg	Atoms	Angles, deg	Atoms	Angles, deg
Polyhedron		Ring I		Ring II	
Br–Mn–N(1)	88.8 (1)	C(2)–N(1)–N(3)	103.7 (3)	C(1)–N(2)–N(4)	103.4 (3)
Br–Mn–N(2)	91.5 (1)	N(1)–N(3)–C(4)	113.3 (3)	N(2)–N(4)–C(7)	113.6 (3)
N(1)–Mn–N(2)	90.9 (1)	N(3)–C(4)–C(3)	105.6 (3)	N(4)–C(7)–C(6)	105.7 (3)
Mn–N(1)–N(3)	122.9 (2)	C(4)–C(3)–C(2)	106.1 (3)	C(7)–C(6)–C(1)	105.9 (4)
Mn–N(1)–C(2)	133.3 (2)	C(3)–C(2)–N(1)	111.3 (3)	C(6)–C(1)–N(2)	111.4 (3)
Mn–N(2)–N(4)	123.6 (2)	C(3)–C(4)–C(5)	132.2 (4)	C(6)–C(7)–C(8)	131.4 (4)
Mn–N(2)–C(1)	133.0 (2)	N(3)–C(4)–C(5)	122.1 (4)	N(4)–C(7)–C(8)	122.9 (4)
Methyl Groups[b,c]		Nitrogen–Hydrogen		Carbon–Hydrogen	
C(4)–C(5)–H_{av}	115 (2)	N(1)–N(3)–H(3)	118 (2)	N(1)–C(2)–H(2)	119 (2)
C(7)–C(8)–H_{av}	105 (2)	N(2)–N(4)–H(4)	119 (3)	N(2)–C(1)–H(1)	118 (3)
H–C(5)–H_{av}	108 (5)	C(4)–N(3)–H(3)	127 (2)	C(1)–C(6)–H(6)	129 (3)
H–C(8)–H_{av}	111 (6)	C(7)–N(4)–H(4)	126 (3)	C(2)–C(3)–H(3)	128 (2)

[a] Only angles of direct bonds have been included. [b] The six C–C–H angles have been averaged; individual values were found to range from 98 to 126°. [c] Two pairs of three H–C–H angles have been averaged; individual values were found from 101 to 114° for C(5) and from 98 to 126° for C(8).

In the molecule, the manganese(II) ion is bonded directly to the four nitrogens N(1), N(2), N(1′), and N(2′) and the two bromine anions Br and Br′. The four heterocyclic rings are related by a symmetry center in two pairs. Only half of the molecule will be considered in the further discussion.

The molecular structure of the asymmetric half of $Mn(mpz)_4Br_2$ is best characterized by two mutually nearly perpendicular five-membered rings, each very close to the plane defined by Mn–Br–N(1) and Mn–Br–N(2), respectively. As can be seen from Table VII the five-membered rings are quite planar, since the atomic deviations from their respective plane are of the same order as their esd's. The C–H bonds at C(3), C(2), C(1), and C(6) are also very close to these planes, as is seen from the angles between the C–H bonds and the planes of 0 ± 2, 2 ± 2, 3 ± 2, and 2 ± 2°, respectively. The N–H bonds, on the other hand, make larger angles with these least-squares planes, *viz.*, 11.6 and 8.6° for N(3)–H and N(4)–H, respectively; this may be due to hydrogen-bond formation (to be discussed below).

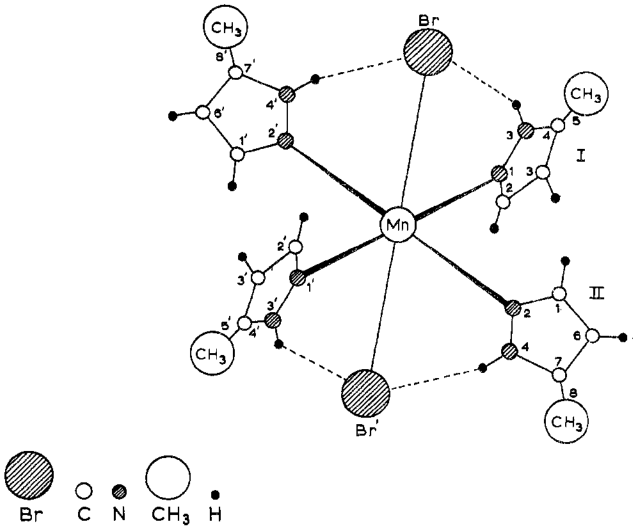

Figure 1.—One molecular unit of $Mn(mpz)_4Br_2$ including numbering of atoms and rings.

The relative orientations of the rings and the anion can best be described by reference to the plane N(1)–N(2)–Mn–N(1′)–N(2′). Each of the five-membered rings intersects this plane, whereas the bromine anions lie above and below this plane. The angle between the Mn–Br bond and this plane is 88.0 (0.1)°, the deviation from 90° being in the direction of the two N–H bonds. Thus, the coordination polyhedron around the Mn(II) ion seems to be slightly distorted from D_{4h} symmetry, first by angles deviating from 90° and second

TABLE VII
LEAST-SQUARES PLANES OF THE HETEROCYCLIC RINGS[a]

Ring I:[b] $0.4144X + 0.8727Y + 0.2584Z + 0.1061 = 0$

Ring II:[b] $-0.9263X + 0.3175Y - 0.2028Z + 0.0846 = 0$

Atom	Dist, Å	Atom	Dist, Å	Atom	Dist, Å	Atom	Dist, Å
N(1)	0.002	C(3)	−0.001	N(2)	0.006	C(6)	−0.001
N(3)	−0.002	C(4)	−0.008	N(4)	−0.007	C(7)	0.007
C(2)	0.003	C(5)	0.006	C(1)	−0.003	C(8)	−0.001

[a] The planes have been calculated giving equal weight to the carbon and nitrogen atoms. [b] The orthogonal axes are defined as in Table VIII, footnote *b*.

by the unequal Mn–N bond lengths (Tables V and VI). Evidence for a slight distortion from D_{4h} symmetry was also obtained from epr spectra[5] of the present compound.

The pyrazole rings I and II′ (see Figure 1) are tilted from the perpendicular positions by 13.0 and 16.9°, respectively, in such a way that the atoms N(3) and N(4′) approach each other at a short distance. *Cf.* N(3)–N(4′) = 3.75 Å with C(1′)–C(2) = 4.81 Å. Further the Mn–N(1) and Mn–N(2) bonds do not coincide with the least-squares planes of rings I and II. The angles between them are 2.6 and 2.0°, respectively. The origin of these features may be the hydrogen bonding (to be discussed below).

From the anisotropic temperature factors of the nonhydrogen atoms the principal axes of the vibrational ellipsoides and their direction cosines with respect to an orthogonal axes system (defined in Table VIII, footnote *b*) were calculated. In this axes system the Mn–Br bond approximately coincides with the *z* axis, whereas ring I is rather close to the *xz* plane and ring II rather close to the *yz* plane. The results are listed in Table VIII. It can be seen from this table that the Mn^{2+} and Br^- ions have their largest thermal motion in directions perpendicular to the Mn–Br bond and between rings I and II. Because of the fact that in each ring the atoms have a common direction for their largest thermal movement (*i.e.*, ring I mainly in the *yz* direction and ring II mainly in the *xy* direction), a rigid-body analysis was applied on the separate rings. The rigid-body analysis according to Cruickshank,[13a] with refinement of the libration center following Pawley,[13b] was chosen and applied to the six carbon and nitrogen atoms of each mpz group.

TABLE VIII

MAGNITUDE OF THERMAL ELLIPSOIDS AND THEIR DIRECTION COSINES[a]

Atom	$(\bar{\mu}_{max}^2)^{1/2}$	Cosines[b]	$(\bar{\mu}_{med}^2)^{1/2}$	Cosines[b]	$(\bar{\mu}_{min}^2)^{1/2}$	Cosines
Mn	0.226	0.0551	0.200	0.5678	0.179	0.8213
		0.8282		−0.4854		0.2800
		0.5577		0.6648		−0.4970
Br	0.255	−0.1653	0.206	−0.9703	0.194	−0.1769
		0.9646		−0.1216		−0.2340
		0.2055		−0.2093		0.9560
N(1)	0.234	0.1659	0.202	0.5538	0.190	0.8159
		0.9547		−0.2975		0.0078
		0.2471		0.7777		−0.5781
N(3)	0.244	0.2733	0.196	0.9492	0.190	0.1562
		0.9345		−0.3005		0.1906
		0.2279		0.0939		−0.9692
C(2)	0.240	−0.1174	0.227	−0.9490	0.193	−0.2926
		−0.8838		−0.0345		0.4665
		−0.4528		0.3134		−0.8347
C(3)	0.246	−0.0286	0.244	−0.5965	0.193	−0.8021
		−0.5443		−0.6640		0.5138
		−0.8384		0.4508		−0.3044
C(4)	0.235	0.0938	0.209	0.5191	0.188	0.8495
		0.5504		0.6840		−0.4787
		−0.8296		0.5125		−0.2216
C(5)	0.294	0.4224	0.268	0.4530	0.203	0.7851
		0.8971		−0.3327		−0.2907
		0.1295		0.8271		−0.5469
N(2)	0.230	−0.1989	0.217	−0.8823	0.194	−0.4265
		0.8914		0.0179		−0.4528
		0.4071		−0.4703		0.7830
N(4)	0.248	−0.9638	0.212	−0.2389	0.195	−0.1187
		0.2661		−0.8934		−0.3619
		−0.0195		−0.3804		0.9246
C(1)	0.299	0.9365	0.244	0.0693	0.201	0.3437
		0.0503		−0.9967		0.0640
		0.3470		−0.0427		−0.9369
C(6)	0.338	−0.9585	0.237	−0.2726	0.210	−0.0840
		0.1070		−0.6165		0.7800
		−0.2644		0.7386		0.6201
C(7)	0.271	0.9526	0.233	0.2138	0.206	0.2163
		−0.1307		−0.3542		0.9260
		0.2746		−0.9104		−0.3094
C(8)	0.428	−0.9536	0.247	0.1581	0.209	0.2564
		−0.1989		−0.3086		0.9302
		0.2262		−0.9380		−0.2628

[a] Expressed as root-mean-square amplitudes. [b] Direction cosines are with respect to an orthogonal axes system, having *x* parallel to $\vec{a}$, *y* parallel to $\vec{c}^* \cdot \vec{a}$, and *z* parallel to $\vec{c}^*$. The sequence is *x*, *y*, *z*.

In ring II the libration center obtained in this way was found to be displaced from the center of gravity, G, to a point midway between G and atom N(2). This is readily understandable, since N(2) is the only ring atom bound to Mn. The axis of the strongest libration is found in the plane of the ring, making about equal angles with the orthogonal $+z$ and $-y$ axes. The second axis also falls in the plane of the molecule, whereas the third axis (with a much weaker libration) is found to be perpendicular to the ring plane. The translational motion of this ring is nearly isotropic.

The mean difference between the observed (Table IV) and calculated U_{ij} values amounts to 0.0026 Å², compared with a mean esd from Table IV of 0.0024 Å². The largest observed difference in U_{ij} is 4 times the esd for that particular U_{ij}. The calculated averaged increase in the bond lengths of the ring amounts to 0.013 Å after the rigid-body correction. The esd of the coordinates of the libration center is 0.1 Å.

A better agreement between observed and calculated U_{ij}'s can be obtained by applying the rigid-body analysis to the five ring atoms only; however in this case the least-squares coordinates of the libration center oscillated too much and could not be refined.

In ring I the tendencies are much the same. The displacement of the libration center, G, however is somewhat more in the direction of the N(3)–N(1) bond. This may be related to the fact that the hydrogen bond N(3)···Br is significantly shorter than N(4)···Br′ (see Table V).

The axis of the strongest libration again falls in the plane of the molecule, in the direction of the orthogonal *x* axis. The second axis now stands perpendicular to the ring plane (*y* axis), whereas the weakest libration occurs in the ring plane, nearly along the *z* axis.

The largest translation of this rigid body was found in the direction of the *y* axis (perpendicular to the ring plane), whereas the remaining translations are equal. The calculated averaged increase of the bond lengths in the ring amounts to 0.006 Å after the rigid-body correction. The smaller value for this increase with respect to that of ring II can be explained by the smaller U_{ij} values for the atoms of ring I. In addition, it may be mentioned that, before the rigid-body correction, the averaged bond lengths in ring I were 0.008 Å longer than those in ring II. Refinement with only five ring atoms did not yield acceptable values for *L* (*e.g.*, negative eigenvalues).

Pyrazole Rings

The bond lengths and bond angles of the pyrazole rings I and II were found to refine to different values, because of the fact that the rings are crystallographically not equivalent. This was found also for two unsub-

(13) (a) D. W. J. Cruickshank, *Acta Crystallogr.*, **9**, 754 (1956); (b) G. S. Pawley, *ibid.*, **16**, 204 (1963).

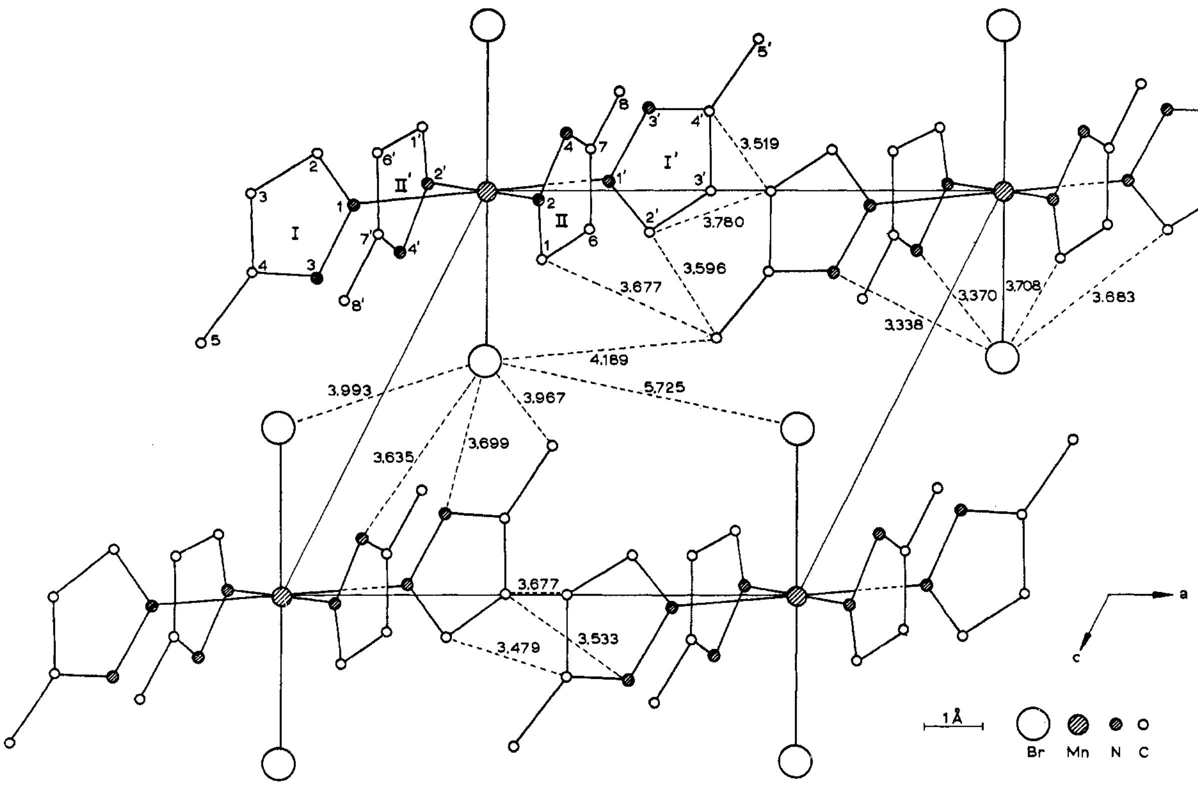

Figure 2.—Packing and intermolecular contacts of $Mn(mpz)_4Br_2$ as viewed down *b*.

stituted pyrazole compounds.[14] However, it can be seen from Tables V and VI that the values found for the bond angles and distances of the two pyrazole rings do not differ significantly. So we can consider rings I and II to be equivalent.

To compare the several bond lengths and angles with literature values[14,15] of the pyrazole ring, Table IX has been compiled. From this table we see that the results available at present are very close together, even for the pyrazolylborato compound.[15b] Thus, the influence of substituents in the pyrazole ring upon bond lengths and bond angles seems to be small.

TABLE IX

COMPARISON OF MEAN BOND LENGTHS (Å) AND BOND ANGLES (DEG) IN PYRAZOLE COMPOUNDS[a]

Distance or angle	$Mn(mpz)_4$-Br_2[b]	$Ni(pz)_4$-Br_2[c]	$Ni(pz)_4$-Cl_2[d]	$Ni(pz)_6$-$(NO_3)_2$[e]	Co(HB-$(pz_3))_2$[f]
N_1–N_2	1.351 (3)[g]	1.344 (9)	1.344 (4)	1.354 (3)	1.364 (6)
N_2–C_3	1.320 (3)	1.322 (6)	1.325 (3)	1.332 (6)	1.330 (6)
C_3–C_4	1.388 (4)	1.389 (9)	1.391 (4)	1.381 (5)	1.393 (7)
C_4–C_5	1.356 (4)	1.351 (11)	1.364 (5)	1.357 (7)	1.379 (7)
C_5–N_1	1.332 (3)	1.354 (8)	1.345 (4)	1.344 (5)	1.339 (6)
C_5–N_1–N_2	113.4 (2)	112.0[h]	111.4 (3)	111.4 (3)	109.9 (4)
N_1–N_2–C_3	103.6 (2)	104.9	105.5 (2)	104.6 (3)	106.0 (4)
N_2–C_3–C_4	111.4 (2)	110.8	110.6 (3)	111.3 (4)	111.2 (5)
C_3–C_4–C_5	106.0 (3)	106.2	105.3 (2)	105.5 (4)	104.1 (4)
C_4–C_5–N_1	105.6 (2)	105.6	107.0 (3)	107.2 (3)	109.0 (5)

[a] The numbering of the ring atoms is that of the organic nomenclature, as presented in the Introduction. [b] Present work. [c] C. W. Reimann and A. Santoro, *Acta Crystallogr., Sect. B*, **25**, 595 (1969). [d] C. W. Reimann, A. D. Mighell, and F. A. Mauer, *ibid.*, **23**, 135 (1967). [e] C. W. Reimann, A. Santoro, and A. D. Mighell, *ibid., Sect. B*, **26**, 521 (1970). [f] M. R. Churchill, K. Gold, and C. E. Maw, *Inorg. Chem.*, **9**, 1597 (1970). [g] Esd's were calculated with the formula $\sigma_m = (\Sigma_{i=1}^{N}\sigma_i)/N^{1.5}$, in which *i* is the *i*th bond angle or length and *N* is the total number. [h] No esd's indicated by the authors.

Intermolecular Contacts

The packing of the molecules within the crystal lattice (viewed along the crystallographic *b* axis) is illustrated in Figure 2. The individual molecules are separated by normal van der Waals distances. The closest contacts are as follows: for ring I–ring I: C···C, 3.48 Å; C···H, 2.90 Å; N···H, 3.19 Å; H···H, 2.67 Å; for ring II–ring II: C···C, 3.73 Å; C···H, 3.10 Å; N···H, larger than 4.0 Å; H···H, 2.74 Å; for ring I–ring II: C···C, 3.68 Å; C···H, 2.88 Å; N···H, 2.77 Å; H···H, 2.56 Å; in addition, the closest Br···H distance was found to be 2.94 Å.

In Figure 2 a few close contacts are indicated (excluding the hydrogen atoms) by dotted lines and printed distances. Generally the closest contacts mainly concern the atoms of ring I. Evidence for this comes also from the root-mean-square vibrational amplitudes (Table VIII) that are much larger for the carbon atoms of ring II than those of ring I. Moreover, the isotropic *B* values of the hydrogens attached to ring II are in general considerably larger than those attached to ring I (Table III).

Hydrogen Bonding

Previous physical measurements[2-5] on the present compound and related ones already suggested the importance of hydrogen bonding in pyrazole complexes. Evidence for hydrogen bonding in $Ni(pz)_4X_2$, with $X^- = Cl^-$ and Br^-, was also demonstrated by X-ray analysis[14] and ligand-field spectra.[16]

It can be seen from Tables V and VI and Figures 1

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(14) (a) C. W. Reimann and A. Santoro, *Acta Crystallogr., Sect. B*, **25**, 595 (1969); (b) C. W. Reimann, A. D. Mighell, and F. A. Mauer, *ibid.*, **23**, 135 (1967).

(15) (a) C. W. Reimann, A. Santoro, and A. D. Mighell, *ibid., Sect. B*, **26**, 521 (1970); (b) M. R. Churchill, K. Gold, and C. E. Maw, *Inorg. Chem.*, **9**, 1597 (1970).

(16) C. W. Reimann, *Chem. Commun.*, 145 (1969).

and 2 that in the present compound hydrogen bonding also plays a role and is responsible for some interesting structural features. (1) There is a movement of the imino nitrogen toward the Br$^-$ ion, as reflected by the Mn–N–N angles of 123° and the Mn–N–C angles of 133°. (2) There is a movement of the Br$^-$ ion from the perpendicular position toward the N–H groups. (3) There are short Br–N distances of 3.34 and 3.37 Å for Br–N(3) and Br–N(4′), respectively, compared with Br–C distances of 3.71 and 3.68 Å for Br–C(1) and Br–C(2′) (see Figure 2 for indicated distances). This feature is of course related to (1) and (2). (4) The orientation of the five-membered rings is nearly perpendicular. A more flattened orientation would be expected on the basis of ligand–ligand repulsions. (5) The rather long Mn–Br bond is 2.727 Å. Comparable literature values for Mn–Br bond lengths are 2.52 Å (in the rather covalent Mn(CO)$_5$Br),[17] 2.49 Å (in five-coordinate Mn(Me$_6$tren)Br$_2$),[18] 2.68 and 2.72 Å (in one-dimensional polymeric MnBr$_2$·2H$_2$O),[19] and 2.72 Å (in the layer structure of MnBr$_2$).[20] (6) The angles of hydrogen bonding N–H···Br are 126 (3)° which seem to be acceptable values.[21]

Finally, we compared the N···Br distances found in the present study with those predicted with the relation of Bellamy and Owen:[22] $\Delta\nu = 50(x^2 - x)$, in which $\Delta\nu$ is the difference in infrared maxima between the gaseous ligand (3540 cm^{-1})[4] and the complexed ligand (3310 cm^{-1})[2] and $x = (d/R)^6$ with $d = 3.95$ Å.[14] This formula predicts $R = 3.35$ Å, whereas values of 3.34 and 3.37 Å are found (Table V).

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The Crystal Structure and Properties of π-Triphenylcyclopropenylchlorodipyridinenickel(0)–Pyridine, a π Complex of a Three-Membered Aromatic Ring

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The crystal and molecular structure of π-triphenylcyclopropenylchlorodipyridinenickel(0)–pyridine, [(π-C$_3$(C$_6$H$_5$)$_3$)NiCl(C$_5$H$_5$N)$_2$]·C$_5$H$_5$N, has been determined from three-dimensional single-crystal X-ray data collected by counter methods. This compound crystallizes as well-separated molecular units in the monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions $a = 16.570$ (3), $b = 10.538$ (1), $c = 22.483$ (5) Å, and $\beta = 129.14$ (1)°. The structure has been refined by full-matrix least-squares methods to a conventional R factor of 0.081 for the 2361 reflections with $I > 2.0\sigma(I)$. When the triphenylcyclopropenyl group is assumed to occupy one coordination position, the coordination geometry about the nickel atom is a distorted tetrahedron. The triphenylcyclopropenyl group is complexed in true π fashion, the three nickel–cyclopropenyl carbon distances being 1.896 (8), 1.958 (8), and 1.968 (8) Å. Carbon–carbon distances in the cyclopropenyl ring are equal within experimental error to an average value of 1.421 (7) Å and are lengthened significantly in this complex compared with the free ligand in (C$_3$(C$_6$H$_5$)$_3$)(ClO$_4$). The nickel–chlorine and average nickel–nitrogen (pyridine) distances are 2.322 (3) and 2.024 (5) Å, respectively.

Introduction

The stability of the cyclopropenium cation as implied by the simple Hückel $4n + 2$ rule ($n = 0$) was confirmed by the synthesis of the triphenylcyclopropenium cation[1] and more recently the parent[2] ion, C$_3$H$_3^+$. However, the first attempts to obtain transition metal π complexes of this aromatic species were unsuccessful.[3,4] In 1964 Gowling and Kettle[5] presented evidence that the reaction of (C$_3$(C$_6$H$_5$)$_3$)Br with Ni(CO)$_4$ gave a dimer complex of the formulation [(π-C$_3$(C$_6$H$_5$)$_3$)NiBr(CO)]$_2$ which contained this carbocyclic ring π bonded to the nickel atom. In order to determine whether this was the mode of bonding and to gain a better understanding of the bonding of small aromatic ring systems to transition metals, an X-ray structural determination of a closely related monomeric derivative,[6] [(π-C$_3$(C$_6$H$_5$)$_3$)NiCl(C$_5$H$_5$N)$_2$]·C$_5$H$_5$N, was undertaken.

Experimental Section

Preparation.[7]—Reaction of the dimeric complex [(π-C$_3$(C$_6$H$_5$)$_3$)-

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