and V reveal no surprises when compared with other polyhedral carborane structures.[9] The Cr atom is situated very nearly exactly over the center of the pentagonal face of each carbollide ion, with the differences in Cr–B and Cr–C bond distances hardly exceeding the standard deviations.

The molecular packing, shown in Figure 3, is dominated by the bulky anions which are close to a body-centered-cubic packing. The cesium ions and water molecules fit into the structure without any strong interactions with neighbors. The water molecule has no neighbors suitable for hydrogen bonding, and therefore it is not surprising that it is observed to have large amplitudes of thermal motion nor that we failed to detect its hydrogen atoms. We cannot exclude the possibility that the large thermal parameters in part reflect incomplete occupancy of the water sites. The thermal parameters listed in Table II correspond to rms displacements along the principal axes: 0.16, 0.21, and 0.25 Å for Cs; 0.36, 0.42, and 0.46 Å for oxygen.

Acknowledgment.—We thank Professor M. Frederick Hawthorne for providing the crystals used in this work.

---

(9) D. St. Clair, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **8**, 2080 (1969); P. T. Greene and R. F. Bryan, *ibid.*, **9**, 1464 (1970); R. W. Rudolph, J. L. Pflug, C. M. Bock, and M. Hodgson, *ibid.*, **9**, 2274 (1970); T. F. Koetzle and W. N. Lipscomb, *ibid.*, **9**, 2279 (1970); D. St. Clair, A. Zalkin, and D. H. Templeton, *J. Amer. Chem. Soc.*, **92**, 1173 (1970); M. R. Churchill and K. Gold, *ibid.*, **92**, 1180 (1970); R. M. Wing, *ibid.*, **92**, 1187 (1970), and references to earlier work found therein.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF ARKANSAS, FAYETTEVILLE, ARKANSAS 72701,
AND CALVIN COLLEGE, GRAND RAPIDS, MICHIGAN 49506

The Crystal and Molecular Structure of Tris(1,2-dimethylhydrazino)diphosphine, $P_2(NCH_3)_6$, a Phosphorus–Nitrogen Cage Molecule

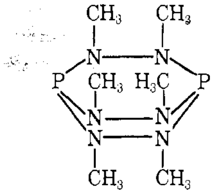
BY WILLIAM VANDOORNE, GARY W. HUNT, RICHARD W. PERRY, AND A. W. CORDES*

Received March 2, 1971

The crystal and molecular structure of the bicyclic tris(1,2-dimethylhydrazino)diphosphine, $P_2(NCH_3)_6$, has been determined by single-crystal X-ray diffraction methods. The unit cell is monoclinic, with $a = 7.312$ (4) Å, $b = 13.361$ (7) Å, $c = 7.133$ (4) Å, $\beta = 116.24$ (1)°, and $d_{\text{calcd}} = 1.256$ g/cm³. The space group is $P2_1/c$ (C_{2h}^5: no. 14), and there are two molecules per unit cell. Diffractometer methods (Mo radiation, λ 0.71069 Å) were used to obtain 261 observed reflections at 23°. Refinement of the structure by full-matrix least-squares methods with isotropic thermal parameters for all atoms gave a final R index of 0.087. The molecule, which consists of three 1,2-dimethylhydrazino groups linking two phosphorus atoms, has nearly threefold symmetry. The crystal is disordered: two enantiomorphs related by an inversion center at the center of the molecule share the same lattice sites. The average P–N, N–N, and N–C bond distances and their rms deviations are 1.68 (3), 1.44 (2), and 1.49 (5) Å, respectively. The NPN, PNN, PNC, and NNC bond angles average 100 (3), 117 (4), 118 (4), and 110 (5)°, respectively. The sum of the angles about the N atoms is 345 (2)°. The P–N–N–P linkages are planar within 0.06 (2) Å, and the carbon atoms are 1.1 (1) Å from these planes. These structural parameters suggest little or no p → d P–N π bonding.

Introduction

Tris(1,2-dimethylhydrazino)diphosphine was first prepared by Payne, Nöth, and Henniger,[1] who proposed a bicyclic structure for this molecule



One feature of interest in this molecule is the extent of π bonding which might prevail in the P–N framework. The general topic of a (p → d)π interaction in P–N bonds of aminophosphines has received considerable attention.[2] The P–N bond distance and the stereochemistry at the nitrogen atoms of $P_2(NCH_3)_6$ provide a good opportunity for obtaining information on the extent of the π bonding in a P–N cage molecule of this type. Completely planar PN(C)N(C)P linkages (sp² N) with P–N distances of 1.59–1.62 Å could be used as evidence for extensive P–N π bonding and would allow only one conformation for this molecule, while nonplanar PN(C)N(C)P units (tetrahedral N) with P–N distances of about 1.77 Å would be expected for a σ-bonded system and would allow the possible existence of a number of isomers differing in the orientations of the methyl groups with respect to the P–N cage.

Collection and Treatment of Data

The sample of $P_2(NCH_3)_6$ was prepared by the method of Payne, Nöth, and Henniger,[1] and crystals were grown by vacuum sublimation. A nearly spherical crystal of radius 0.14 (1) mm was sealed in a Lindemann capillary with a parallel to the ϕ axis. All handling of the crystal was done under an atmosphere of dry nitrogen. Preliminary Weissenberg photographs showed Laue symmetry and systematic absences which uniquely indicated space group $P2_1/c$. The diffractometer data were obtained with a GE XRD-5 manually operated unit using Mo Kα (λ 0.71069 Å) radiation filtered with 1-mil zirconium foil, a scintillation counter, and a pulse height analyzer set for a 90% window. Least-squares refinement[3] of the setting angles of 13 carefully centered reflections gave the following cell parameters at

---

[1] D. S. Payne, H. Nöth, and G. Henniger, *Chem. Commun.*, 327 (1965).

[2] *Cf.* A. B. Burg, *Accounts Chem. Res.*, **2**, 353 (1969); A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, **92**, 5206 (1970); J. E. Smith, R. Steen, and K. Cohn, *ibid.*, **92**, 6359 (1970), and references therein.

[3] A. Foust, Program ANGSET, University of Wisconsin, 1968.

23°: $a = 7.312$ (4) Å, $b = 13.361$ (7) Å, $c = 7.133$ (4) Å, and $\beta = 116.24$ (1) Å. Because the compound is very soluble in organic solvents and is extremely sensitive to moisture, the crystal density was not determined. The most reasonable density (1.256 g cm^{-3}) for the crystal is that calculated when the number of molecules per unit cell is assumed to be 2.

For intensity data collection each reflection was scanned 2° with a θ–2θ scan at a scan rate of 2°/min with a takeoff angle of 3°. Stationary crystal–stationary counter background readings were taken for 10 sec at each end of the scans. All peaks with $0° \leq 2\theta < 40°$ were scanned. Only a few reflections with $2\theta > 35°$ had intensities above background. There are 635 possible reflections in the Mo Kα sphere bounded by $2\theta < 40°$; we found 316 reflections had intensities greater than one standard deviation and 265 of these had intensities greater than two standard deviations. The latter reflections, with four omissions, were used for the structure determination and refinement. The omissions were three reflections (011, 11−1, and 020) which were so intense they swamped the counter, and the 400 reflection which had a severe background imbalance. The standard deviations were calculated by $\sigma_I = (S + BT^2 + 0.0016I^2)^{1/2}$ (where S = total scan count, B = sum of the background counts, T = (scan time)/(total background time), and $I = S - BT$), except for a small number of reflections for which the two background readings differed by more than twice the calculated σ due to tailing of the reflection peak. For the latter reflections the standard deviations were set equal to the deviation of the background readings from the mean background value.

Four reflections were measured periodically during data collection as a monitor of crystal and electronic stability. A gradual decrease in the intensity of all four of these reflections indicated the diffracting power of the crystal fell off as a linear function of total elapsed time (as opposed to radiation time). The total drop of the intensity of the check reflections from start to finish of data collection (4 days) was 15% or 4σ. A simple linear correction was made.

No absorption correction was made ($\mu = 2.62$ cm^{-1} and $\mu r = 0.05$), nor were extinction corrections attempted. Scattering factors for neutral elements were calculated from the analytical functions of Cromer and Mann,[4] and real and imaginary anomalous scattering corrections were made for the phosphorus atom.[5]

Solution and Refinement of the Structure

In refining the structure by least-squares methods, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = ((I_o + \sigma(I_o))^{1/2} - F_o)^{-2}$ and the R factors are defined as $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w||F_o| - |F_c||^2/\Sigma w F_o^2)^{1/2}$. The Fourier program was written in our laboratory, and the least-squares program was a modified version of ORFLS. Two molecules per unit cell in space group $P2_1/c$ requires the center of the molecules to lie on crystallographic inversion centers. Since the expected molecular structure was not centrosymmetric, disorder was indicated. A three-dimensional Patterson function revealed the location of the phosphorus atoms, and a three-dimensional Fourier map, phased by the phosphorus atoms ($R_1 = 0.367$), showed six nitrogen atoms 1.7 Å from each phosphorus, instead of the expected three, because of disorder in the system. Each nitrogen atom was therefore assigned a multiplicity factor of 0.5 during all subsequent operations in solving the structure.

The remaining peaks in the Fourier map were assigned to carbon atoms. There were only the expected six carbon atoms per molecule; a model revealed the carbon positions could nearly serve both of the disordered P–N frameworks (see Figure 1).

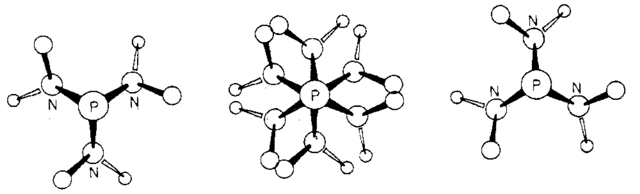


Figure 1.—Idealized drawing of the two isomers of $P_2(NCH_3)_6$, showing the relative positions in the disordered crystal. View is down the molecular axis. The individual isomers are shown at the left and right and are superimposed in the central figure.

Several cycles of least-squares refinement using isotropic temperature factors for all atoms gave $R_1 = 0.12$ and $R_2 = 0.13$. High thermal parameters for the carbon atoms indicated the accidental overlap of the two half-populated carbon positions was not the true solution, so the carbon positions were separated along a line parallel to the line joining the two nearest nitrogen atoms (Table I). This carbon–carbon separation eventually refined to about 0.5 Å (see Table II).

TABLE I[a]

FINAL ATOMIC POSITIONAL AND THERMAL PARAMETERS FOR $P_2(NCH_3)_6$

Atom	x	y	z	B, Å^2
P	0.1417 (8)	0.0464 (4)	0.2033 (8)	5.5 (2)
N(1)	0.229 (3)	−0.050 (2)	0.103 (3)	4.1 (5)
N(2)	0.031 (4)	0.116 (2)	−0.018 (4)	4.6 (6)
N(3)	−0.075 (4)	−0.008 (2)	0.182 (4)	4.9 (6)
N(4)	0.106 (4)	−0.084 (2)	−0.103 (4)	5.2 (7)
N(5)	−0.118 (4)	0.076 (2)	−0.215 (4)	5.1 (6)
N(6)	−0.198 (4)	−0.064 (2)	−0.007 (4)	5.4 (6)
C(1)	0.331 (5)	−0.130 (3)	0.241 (5)	2.8 (9)
C(2)	0.171 (9)	0.180 (4)	−0.087 (8)	6.8 (18)
C(3)	−0.210 (10)	0.052 (5)	0.248 (11)	6.8 (26)
C(4)	0.219 (10)	−0.080 (5)	−0.235 (10)	6.2 (23)
C(5)	−0.290 (6)	0.114 (3)	−0.312 (6)	5.8 (12)
C(6)	−0.235 (8)	−0.176 (4)	0.022 (8)	6.8 (18)

[a] In all tables, the numbers in parentheses are the standard deviations in the least significant digits.

TABLE II

SELECTED INTRAMOLECULAR DISTANCES (Å) AND ANGLES (DEG) IN $P_2(NCH_3)_6$

	Distance		
P–N(1)	1.72 (3)	N(1)–C(1)	1.43 (4)
P–N(2)	1.69 (3)	N(2)–C(2)	1.57 (6)
P–N(3)	1.69 (3)	N(3)–C(3)	1.51 (7)
P′–N(4)	1.70 (3)	N(4)–C(4)	1.50 (7)
P′–N(5)	1.65 (2)	N(5)–C(5)	1.46 (5)
P′–N(6)	1.64 (2)	N(6)–C(6)	1.55 (6)
P–N (av)[a]	1.68 (3)	N–C (av)[a]	1.49 (5)
N(1)–N(4)	1.42 (4)	C(1)–C(5)′[b]	0.72 (6)
N(2)–N(5)	1.45 (4)	C(2)–C(6)′	0.49 (9)
N(3)–N(6)	1.45 (4)	C(3)–C(4)′	0.38 (9)
N–N (av)[a]	1.44 (2)	C–C (av)[a]	0.5 (2)
	Angle		
N(1)–P–N(2)	98 (1)	P–N(1)–C(1)	117 (2)
N(1)–P–N(3)	98 (1)	P–N(2)–C(2)	119 (2)
N(2)–P–N(3)	96 (1)	P–N(3)–C(3)	117 (3)
N(4)–P′–N(5)	101 (1)	P′–N(4)–C(4)	121 (3)
N(4)–P′–N(6)	103 (1)	P′–N(5)–C(5)	123 (2)
N(5)–P′–N(6)	105 (1)	P′–N(6)–C(6)	112 (2)
N–P–N (av)[a]	100 (3)	P–N–C (av)[a]	118 (4)
P–N(1)–N(4)	119 (1)	N(4)–N(1)–C(1)	111 (2)
P–N(2)–N(5)	123 (2)	N(5)–N(2)–C(2)	102 (3)
P–N(3)–N(6)	119 (1)	N(6)–N(3)–C(3)	111 (3)
P′–N(4)–N(1)	114 (1)	N(1)–N(4)–N(4)	111 (3)
P′–N(5)–N(2)	111 (2)	N(2)–N(5)–N(5)	111 (3)
P′–N(6)–N(3)	115 (2)	N(3)–N(6)–C(6)	116 (3)
P–N–N (av)[a]	117 (4)	N–N–C (av)[a]	110 (5)

[a] Average distances and angles are weighted averages. The deviations for the average values are the root-mean-square deviations of the contributing values. [b] The primed symbols are related to the positions of Table II by $-x, -y, -z$.

Final refinement reduced the values of R_1 and R_2 to 0.087 and 0.093, respectively. Attempts to include anisotropic thermal parameters for the phosphorus atom did not lower these R values a significant amount,[6] and it was felt such a refinement was overtaxing the data. Refinement of the multiplicity of the fractionally populated atom positions showed 0.5 multiplicity was best. The standard deviation of an observation of unit weight is 1.57. In the final cycle of refinement, all parameter shifts were

---

[4] D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1969).

[5] D. T. Cromer, *ibid.*, **18**, 17 (1965).

[6] W. C. Hamilton, *ibid.*, **18**, 502 (1965).

less than 0.13 of their estimated standard deviation.[7] A final three-dimensional difference Fourier map showed no peaks greater than 0.25 $e^-/Å^3$ (9% of the value observed for a carbon atom) and did not permit location of the methyl hydrogen atoms.

At the completion of the centrosymmetric refinement a noncentrosymmetric structure, without the disorder, was refined using space group Pc. The isotropic refinement, however, gave R values which were 1–2% higher than the $P2_1/c$ refinement in spite of the fact that more positional parameters were required in the noncentrosymmetric case. All estimated standard deviations for positional and thermal parameters were at least 50% higher in the noncentrosymmetric refinement. The choice of a centrosymmetric space group was also supported by the statistical distribution of E values.

Results and Discussion

An idealized drawing of the two enantiomers which are centered at 0, 0, 0 and 0, $^1/_2$, $^1/_2$ in the unit cell is shown in Figure 1. The packing of the neutral molecules is governed largely by the packing of the methyl groups which form the outer "shell" of the rather spherical molecules. Since both isomers utilize nearly the same positions in the unit cell for the methyl groups, the disorder of the N framework within the molecule is probably accompanied by a very small change in the lattice energy. There were no intermolecular contacts significantly shorter than the corresponding van der Waals distances; C(5) was involved in the three shortest C···C distances of 3.61 and 3.72 Å (with C(4)) and 3.64 Å (with C(3)). The crystal packing is shown in Figure 2.

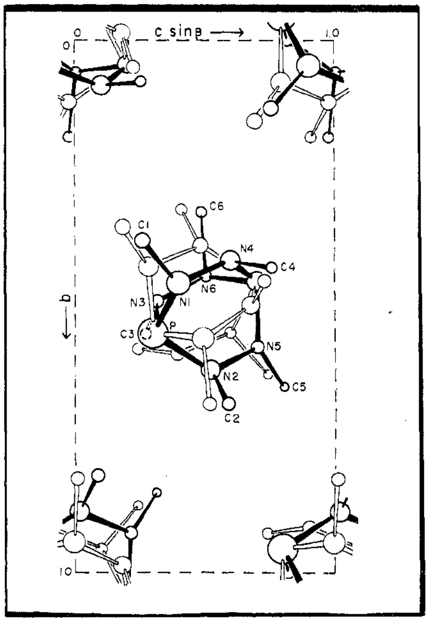


Figure 2.—Packing diagram of $P_2(NCH_3)_6$. The crystal structure is viewed down the a axis. One isomer is connected with blackened tapers; the other, with open tapers.

Each isomer consists of two phosphorus atoms connected by three bridging dimethylhydrazine groups. Each P–N–N–P linkage is planar within 0.08 Å (less than two standard deviations), and the methyl carbon atoms attached to the nitrogens average 1.13 Å from these planes (see Table III). Thus the methyl groups are in a staggered position and destroy the four mirror planes crudely obeyed by the P_2N_6 framework.

TABLE III

LEAST-SQUARES PLANES WITHIN $P_2(NCH_3)_6$[a–c]

Atom	Dist, Å	Atom	Dist, Å
(A) $0.3358X + 0.8476Y - 0.4109Z = 0.00020$			
P	0.04	N(4)	0.08
P′	0.04	C(1)	1.10
N(1)	0.08	C(4)	1.16
(B) $0.8147X - 0.2603Y - 0.5183Z = -0.00007$			
P	0.02	N(5)	0.03
P′	0.02	C(2)	1.18
N(2)	0.04	C(4)	0.97
(C) $-0.2775X + 0.9599Y - 0.0395Z = 0.00007$			
P	0.03	N(6)	0.07
P′	0.03	C(3)	1.16
N(3)	0.07	C(6)	1.22

[a] All planes are expressed in the monoclinic crystal coordinate system. [b] The planes were derived using unit weights for phosphorus and nitrogen atoms and zero weights for the carbon atoms. [c] A primed symbol is related by $-x$, $-y$, $-z$ to the unprimed atom.

The bond distances and angles, their estimated standard deviations, and the weighted average of each bond type are given in Table II. The high standard deviations are probably due to the small amount of data and the disorder problem.

The average N–N bond distance of 1.44 (2) Å is well within statistical error of the 1.449 (4) Å N–N distance of hydrazine determined by electron diffraction.[8] The average nitrogen–carbon bond length of 1.49 (5) Å compares to the normal 1.472 (5) Å distance for paraffinic carbon to three-covalent-nitrogen bonds.[9]

Considering only those compounds in which the phosphorus is bonded to a three-coordinated nitrogen atom, noncyclic P–N bond lengths vary from 1.769 (19) Å in the $H_2NP(OH)O_2^-$ ion[10] (a value often quoted as the bond distance of a single P–N bond) to 1.628 (5)[11] and 1.593 (6) Å in $F_2PN(CH_3)_2$.[12] The average P–N value of 1.68 (3) Å in $P_2(NCH_3)_6$ is between the abovementioned extremes and is comparable to the two P–exocyclic N bonds of $N_4P_4(N(CH_3)_2)_8$[13] (1.67 (1) and 1.69 (1) Å) and the 1.653 (5) Å P–N distance of $(H_2N)_3PBH_3$.[14]

The molecular structure does not give strong support for extensive pπ–dπ P–N bonding. Although the P–N bond lengths are comparable to P–N bonds which are assumed to have appreciable π character [$(H_2N)_3PBH_3$ and the two exocyclic bonds of $N_4P_4(N(CH_3)_2)_8$], the stereochemistry of the nitrogen does not support an sp^2 π-bonding conclusion. In the latter compounds the three bonds of the nitrogen are essentially coplanar (angle sums of 360, 349.5, and 358.4°, respectively), whereas the average sum of the N angles in $P_2(NCH_3)_6$ is 345 (1)°.

The lack of shortening of the N–N bond from the hydrazine value should also be noted as evidence against

---

[7] 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 $3.00 for photocopy or $2.00 for microfiche.

(8) Y. Morino, T. Iijima, and Y. Murata, *Bull. Chem. Soc. Jap.*, **33**, 46 (1960).

(9) L. E. Sutton, "Table of Interatomic Distances and Configuration in Molecules and Ions," Supplement 1956–1959, The Chemical Society, London, 1965.

(10) E. Hobbs, D. E. C. Corbridge, and B. Raistrick, *Acta Crystallogr.*, **6**, 621 (1953).

(11) E. D. Morris and C. E. Nordman, *Inorg. Chem.*, **8**, 1673 (1969).

(12) M. D. LaPrade and C. E. Nordman, *ibid.*, **8**, 1669 (1969).

(13) G. J. Bullen, *J. Chem. Soc.*, 3193 (1962).

(14) C. E. Nordman, *Acta Crystallogr.*, **13**, 535 (1960).

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), $Mn(C_4H_6N_2)_4Br_2$

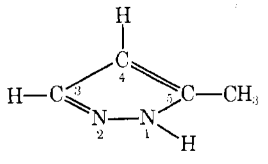
BY J. REEDIJK,* B. A. STORK-BLAISSE, AND G. C. VERSCHOOR

Received March 9, 1971

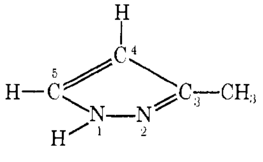
The crystal and molecular structure of dibromotetrakis(5-methylpyrazole)manganese(II), $Mn(C_4H_6N_2)_4Br_2$, has been determined by single-crystal X-ray diffraction techniques. The compound crystallizes in the triclinic system, space group $P\bar{1}$, with a = 8.802 (6) Å, b = 9.695 (5) Å, c = 7.613 (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/cm³ agrees with a value of 1.593 g/cm³ 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).