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# The Crystal Structure of Catena-μ-dichlorobis(pyrazole)manganese(II), $[MnCl_2(C_3H_4N_2)_2]_\infty$

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The crystal structure has been determined by single-crystal X-ray diffraction techniques. The compound is monoclinic, space group $C2/c$ with $a=18{\cdot}26$ (2), $b=3{\cdot}761$ (2), $c=13{\cdot}839$ (2) Å, $\beta=94{\cdot}78$ (8)° and $Z=4$. Data to $(\sin\theta)/\lambda=0{\cdot}81$ Å$^{-1}$ (Mo $K\alpha$ radiation) were collected with a three-circle diffractometer and the structure was solved by means of the Patterson synthesis and refined by least-squares methods to a final conventional $R$ value of 0·046 for 1496 observed reflexions. The compound contains rows of bis(pyrazole)manganese(II) units bridged by chlorine atoms. The rows are separated by normal van der Waals distances. The coordination polyhedron around manganese has $C_2$ symmetry and comprises two nitrogen atoms of the pyrazole ligands and four chlorine atoms.

## Introduction

In previous work of this laboratory (Witteveen & Reedijk, 1973) it was found that the magnetic properties of dichlorobis(pyrazole)manganese(II) [hereinafter called $Mn(pz)_2Cl_2$] could only be understood if this compound was built up of rows containing manganese bridged by chlorine atoms. To test the validity of this idea the crystal structure of $Mn(pz)_2Cl_2$ has been determined.

## Unit cell and space group

Crystals of $Mn(pz)_2Cl_2$ were obtained from alcoholic solutions of $MnCl_2(H_2O)_4$ and the stoichiometric amount of pyrazole, followed by recrystallization from hot alcoholic solution, as described previously (Reedijk, 1970). Crystal symmetry and approximate cell parameters were determined from zero- and upper-level Weissenberg photographs. The diffraction pattern exhibited Laue group $2/m$ and systematic extinctions for $hkl$, $h+k$ odd, and for $h0l$ ($h$), $l$ odd, which indicate the space groups $C2/c$ or $Cc$. The consistency of the results justified the initially chosen space group $C2/c$. Precise unit-cell parameters were determined on a single-crystal diffractometer at 20 °C, with Mo $K\alpha$ radiation ($\lambda=0{\cdot}71069$ Å). The parameters, $a=18{\cdot}26(2)$, $b=3{\cdot}761(2)$, $c=13{\cdot}839(2)$, $\beta=94{\cdot}78(8)$°, were obtained from $\theta,\varphi$ and $\chi$ measurements of 14 $h00$, $0k0$ and $00l$ reflexions. The density of 1·832(3) g cm$^{-3}$, measured by the flotation method in $CCl_4$–$CH_3I$, agrees with a value of 1·838 g cm$^{-3}$ calculated for $Z=4$ and a molecular weight of 262·00.

## Collection and reduction of X-ray diffraction data

A crystal of approximate size 0·2 × 0·23 × 0·18 mm with well developed (100), (010) and (001) faces was mounted on an Enraf–Nonius three-circle single-crystal diffractometer, with the plane $(\bar{1}04)$ perpendicular to the $\varphi$ axis. Intensities were recorded by the $\theta$–$2\theta$ scan method for all reflexions with $\theta$ between 4° and 35°. Mo $K\alpha$ radiation monochromatized by graphite was used. Background intensities were determined at $\theta\pm\frac{1}{2}\Delta$ with $\Delta=0{\cdot}8+0{\cdot}85\tan\theta$. The mean counting time was 26 s for each background and 52 s for the scan.

2444 reflexions were measured, of which 1509 had intensities greater than twice their standard deviation ($\sigma$); these $\sigma$'s were calculated from counting statistics of the measurements. The observed data were corrected for Lorentz and polarization effects. At a later stage absorption corrections were also applied, by use of the modified Monte Carlo method of de Graaff (1973). Calculated transmission factors lay between 0·64 and 0·73 ($\mu=17{\cdot}83$cm$^{-1}$). After reduction of the intensities to $F$ values, a Wilson plot was calculated from which were obtained approximate values for the scale factor and the initial overall isotropic thermal parameter $B$; $F(000)=524$ on an absolute scale.

## Solution and refinement

If one accepts the centrosymmetric space group $C2/c$ the manganese atoms must occur either at centres of symmetry or on twofold axes (*International Tables for X-ray Crystallography*, 1965). The three-dimensional Patterson synthesis was interpretable for both alternatives and its analysis gave positions for all atoms except hydrogen. A full-matrix refinement of positional coordinates and individual isotropic thermal parameters for 13 non-hydrogen atoms and Mn at 0,0,0 (centre of symmetry) converged to the rather high value $R=0{\cdot}146$. A difference synthesis phased by these atoms indicated that the choice of special position for manganese had not been correct. We then tried the alternative with Mn at $0,y,\frac{1}{4}$ (twofold axis). Three cycles of full-matrix refinement of positional parameters and individual isotropic thermal parameters of the non-hydrogen atoms resulted in $R=0{\cdot}108$. Three additional cycles of full-matrix refinement including individual anisotropic thermal parameters led to $R=0{\cdot}065$.

A difference synthesis phased by the non-hydrogen atoms with their new positional parameters revealed the positions of the hydrogen atoms. Three more cycles of full-matrix refinement led to convergence at $R=0{\cdot}058$ ($R_w=0{\cdot}098$). At this stage an extinction correction was applied to the diffraction data. Six new cycles of least-squares refinement, applying anisotropic thermal parameters for all non-hydrogen atoms, yielded $R=0{\cdot}052$ ($R_w=0{\cdot}089$). Next a difference synthesis showed small peaks (about 1 e Å$^{-3}$) in the vicinity of manganese. Since scattering factors for neutral atoms had so far been used, we investigated the influence of scattering factors for manganese(II) and chloride ions. They led to the same value for $R$. Inspection of the measurements showed that the reflexions $h016$ had been measured with a wrong position of $\chi$ and they were accordingly omitted.

Finally four additional cycles led to $R=0{\cdot}046$ ($R_w=0{\cdot}072$). Since in the last cycle the parameter shifts were less than 1/25th of the estimated standard deviations the refinement was considered to be finished.

The final difference synthesis had only small peaks in the vicinity of Mn, which may be due partly to the fact that the imaginary part of the dispersion correction was not allowed for. Observed and calculated structure factors are shown in Table 1. Atomic parameters are collected in Tables 2 and 3. The anisotropic thermal parameters for the non-hydrogen atoms are listed in Table 4.

Scattering factors, taken from Cromer & Waber (1965) and from Stewart, Davidson & Simpson (1965), were used after correction for the real part of the anomalous dispersion, $\Delta f'$.

The function minimized during the least-squares refinement process was $\sum w(|F_o|-|F_c|)^2$, with the weighting scheme $w=1/\sigma_F^2$. Discrepancy indices refer to $R=\sum||F_o|-|F_c||/\sum|F_o|$ and $R_w=\{\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2\}^{1/2}$.

Table 1. *Observed and calculated structure factors on an absolute scale* (× 10)

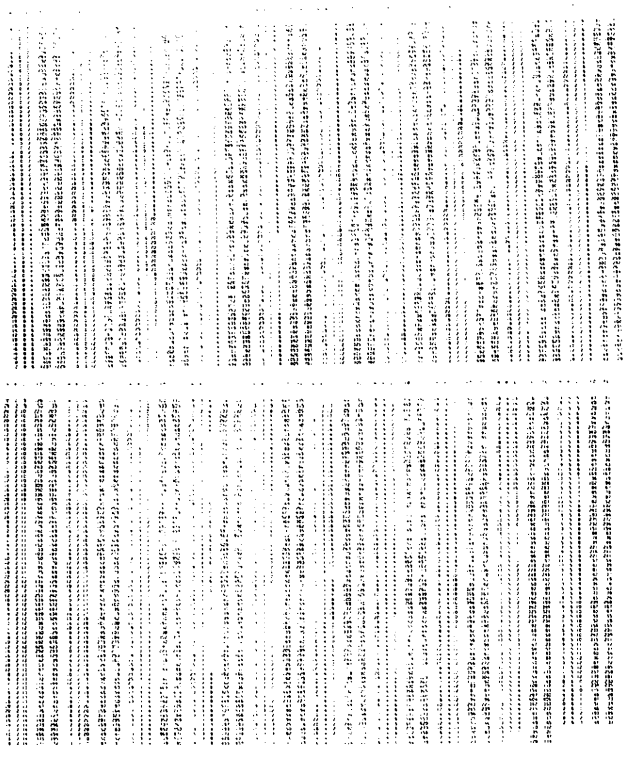

Table 2. *Fractional coordinates of the non-hydrogen atoms*

Estimated standard deviations (e.s.d.'s) in the least significant digits are in parentheses for this and following tables.
The numbers in parentheses correspond to the IUPAC numbering of the ring atoms.

| | *x* | *y* | *z* |
|---|---|---|---|
| Mn | 0·0 | 0·0070 (2) | 0·2500 |
| Cl | 0·05252 (4) | 0·5066 (2) | 0·36481 (4) |
| N(1) | 0·1012 (2) | −0·1183 (8) | 0·0803 (2) |
| N(2) | 0·0999 (1) | −0·0006 (6) | 0·1713 (2) |
| C(3) | 0·1672 (2) | 0·1287 (9) | 0·1938 (2) |
| C(4) | 0·2108 (2) | 0·0892 (9) | 0·1164 (3) |
| C(5) | 0·1670 (2) | −0·0686 (9) | 0·0464 (2) |

Table 3. *Positional and isotropic temperature parameters for the hydrogen atoms*

The numbers in parentheses are those of the ring atoms to which the hydrogen atoms are attached.

| | *x* | *y* | *z* | *B*(Å$^2$) |
|---|---|---|---|---|
| H(1) | 0·065 (2) | −0·22 (1) | 0·055 (3) | 3 (1) |
| H(3) | 0·176 (3) | 0·22 (2) | 0·255 (4) | 7 (2) |
| H(4) | 0·256 (2) | 0·15 (1) | 0·123 (2) | 2 (1) |
| H(5) | 0·180 (2) | −0·14 (1) | −0·032 (3) | 5 (1) |

## The molecular structure

Intramolecular distances and their estimated standard deviations (e.s.d.'s) are shown in Table 5, and bond angles with e.s.d.'s in Table 6. The stereochemistry of

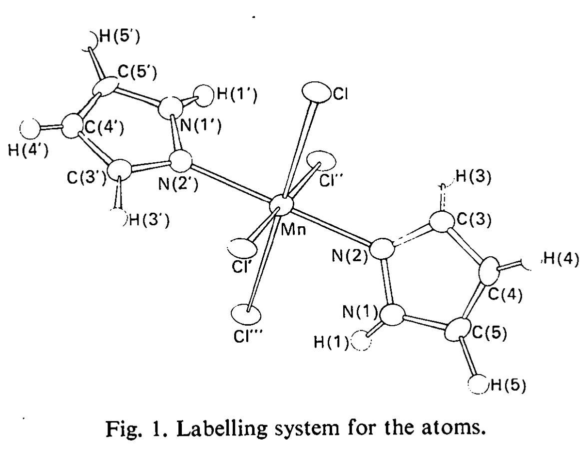

Fig. 1. Labelling system for the atoms.

$Mn(pz)_2Cl_2$ and the atomic labelling are depicted in Fig. 1. Each manganese atom is bonded directly to two nitrogen atoms [N(2) and N(2′)] and four chlorine atoms.

The two heterocyclic rings are related by a twofold axis. As can be seen from Table 7, the five-membered ring is planar within 0·003 Å. The C–H bonds at C(3), C(4), C(5) and the N–H bond at N(1) are also very close to this plane, as can be seen from the angles they make with the pyrazole ring [0(3)°,3(2)°,2(3)° and 3(4)°, respectively].

The relative orientations of the rings and Mn can best be described by reference to the *XZ*-plane of the cell (*cf.* Fig. 2). The plane defined by manganese and four surrounding chlorine atoms is perpendicular to this plane. The angle between the pyrazole ring and the *XZ*-plane is 26·1°. The Mn–N(2) and Mn–N(2′) bonds are not collinear, their angle being 178·5°. Moreover, the plane Cl–Mn–Cl′ is not perpendicular to the plane N(2)–Mn–N(2′): the angle between the Mn–N(2) bond and the Cl–Mn–Cl′ plane is 87·9°.

Although the deviations from $D_{4h}$ symmetry are small, the coordination symmetry of Mn is strictly only $C_2$.

The geometry of the compound can best be described as consisting of rows of manganese in the direction [010]. Consecutive metal atoms are bridged by two chlorine atoms in such a way that a chain is formed (*cf.* Fig. 3). Neighbouring chains are displaced by $\frac{1}{2}00$, $-\frac{1}{2}00$, $00\frac{1}{2}$ and $00-\frac{1}{2}$.

Table 5. *Intramolecular distances* (Å) *and their e.s.d.'s*

The e.s.d.'s in distances include those in cell parameters. The atoms marked with a prime are related to the atoms with the same number by a twofold axis.

| | | | |
|---|---|---|---|
| Mn——Cl | 2·592 (2) | N(2)–C(3) | 1·334 (4) |
| Mn——Cl″* | 2·594 (2) | C(3)–C(4) | 1·395 (5) |
| Mn——N(2) | 2·201 (3) | C(4)–C(5) | 1·342 (5) |
| Mn···N(1) | 3·143 (3) | C(5)–N(1) | 1·339 (4) |
| Mn···C(3) | 3·245 (3) | C(3)–H(3) | 0·91 (6) |
| Cl····N(2) | 3·456 (3) | C(4)–H(4) | 0·86 (4) |
| Cl····N(2′) | 3·377 (3) | C(5)–H(5) | 1·16 (5) |
| Cl····Cl′ | 3·572 (1) | N(1)–H(1) | 0·82 (4) |
| N(1)—N(2) | 1·337 (4) | | |

*Cl″ is related to Cl by a translation of $[0\bar{1}0]$.

Table 4. *Anisotropic temperature factors of non-hydrogen atoms* (Å$^2$)

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $2U_{12}$ | $2U_{23}$ | $2U_{31}$ |
|---|---|---|---|---|---|---|
| Mn | 0·0271 (3) | 0·0216 (3) | 0·0216 (3) | 0·0 | 0·0 | 0·0128 (4) |
| Cl | 0·0342 (4) | 0·0228 (3) | 0·0213 (3) | −0·0042 (6) | 0·0002 (5) | −0·0028 (5) |
| N(1) | 0·031 (1) | 0·034 (1) | 0·022 (1) | −0·006 (2) | −0·007 (2) | 0·005 (2) |
| N(2) | 0·028 (1) | 0·028 (1) | 0·023 (1) | 0·002 (2) | −0·007 (2) | 0·007 (2) |
| C(3) | 0·033 (1) | 0·034 (1) | 0·026 (1) | −0·008 (3) | −0·007 (2) | 0·007 (2) |
| C(4) | 0·030 (1) | 0·035 (2) | 0·039 (2) | −0·005 (3) | 0·011 (3) | 0·019 (3) |
| C(5) | 0·041 (2) | 0·038 (2) | 0·026 (1) | 0·005 (3) | 0·007 (2) | 0·032 (2) |

The general anisotropic temperature factor has the form exp $\{-2\pi^2(\sum_i\sum_j U_{ij}h_ih_ja_i^*a_j^*)\}$.

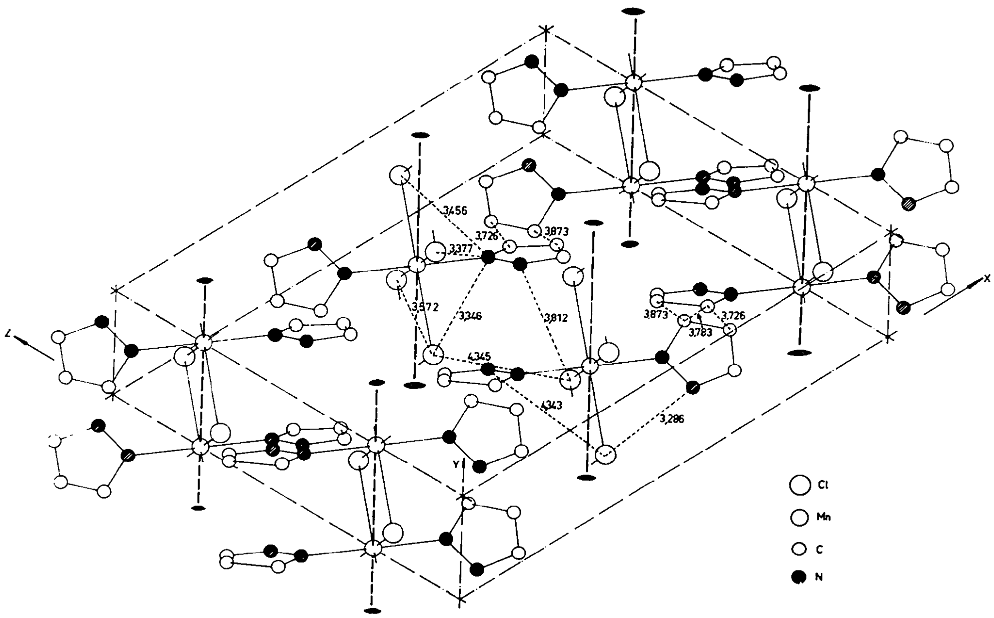

Fig. 2. Packing and intermolecular contacts of $[Mn(pz)_2(Cl_2]_\infty$.

Table 6. *Bond angles (°) and their e.s.d.'s*

| Polyhedron | | Nitrogen–hydrogen | |
|---|---|---|---|
| Cl—Mn—N(2) | 91·9 (3) | N(2)–N(1)–H(1) | 118 (2) |
| Cl—Mn—N(2′) | 89·2 (3) | C(5)–N(1)–H(1) | 129 (2) |
| Cl—Mn—Cl′ | 87·1 (1) | | |
| N(2)–Mn—N(2′) | 178·5 (3) | Carbon–hydrogen | |
| N(1)–N(2)–Mn | 123·5 (4) | N(2)–C(3)–H(3) | 116 (3) |
| C(3)–N(2)–Mn | 131·7 (4) | C(4)–C(3)–H(3) | 133 (3) |
| | | C(3)–C(4)–H(4) | 120 (2) |
| Ring | | C(5)–C(4)–H(4) | 135 (2) |
| N(1)–N(2)–C(2) | 104·6 (4) | N(1)–C(5)–H(5) | 124 (2) |
| N(2)–N(1)–C(5) | 111·8 (5) | C(4)–C(5)–H(5) | 128 (2) |
| N(2)–C(3)–C(4) | 110·9 (5) | | |
| C(3)–C(4)–C(5) | 104·9 (5) | | |
| N(1)–C(5)–C(4) | 107·9 (5) | | |

Table 7. *Least-squares plane of the heterocyclic ring and atomic deviations* (Å)

Plane function: $-0{\cdot}2702X+0{\cdot}8975Y-0{\cdot}3484Z+1{\cdot}2625=0^*$

| | | | |
|---|---|---|---|
| N(1) | 0·003 | C(3) | 0·001 |
| N(2) | −0·002 | C(4) | 0·000 |
| | | C(5) | −0·002 |

$$^*\begin{pmatrix}1 & 0 & \cos\beta\\ 0 & 1 & 0\\ 0 & 0 & \sin\beta\end{pmatrix}\begin{pmatrix}a\\ b\\ c\end{pmatrix}=\begin{pmatrix}X\\ Y\\ Z\end{pmatrix}$$

## Pyrazole rings

The bond lengths and angles of the pyrazole ring are given in Tables 5 and 6 and compared with literature values in Table 8. Note that the results available at present are very similar, even for the pyrazolylborato compound.

### *Intermolecular contacts*

The packing of the chains within the crystal lattice is depicted in Fig. 2. The individual chains are separated by normal van der Waals distances. A few close contacts between non-hydrogen atoms are indicated by dotted lines and their lengths are given in this figure.

## Hydrogen bonding

Hamilton & Ibers (1968) have reported a number of $H\cdots Cl^-$ and $N\cdots Cl^-$ distances as well as $N{-}H\cdots Cl^-$ angles which might characterize an $N{-}H\cdots Cl^-$ bond. The mean values are given below, together with our values for $N(1){-}H(1)\cdots Cl^{iii}$ and $N(1){-}H(1)\cdots Cl^{iv}$ (Table 9), where $Cl^{iii}$ and $Cl^{iv}$ are related to Cl by the operations $\bar{x},y-1,\frac{1}{2}-z$ and $x,\bar{y},z-\frac{1}{2}$ respectively.

We state that both $N(1){-}H(1)\cdots Cl^{iii}$ and $N(1){-}H(1)\cdots Cl^{iv}$ are hydrogen bonds, although the values

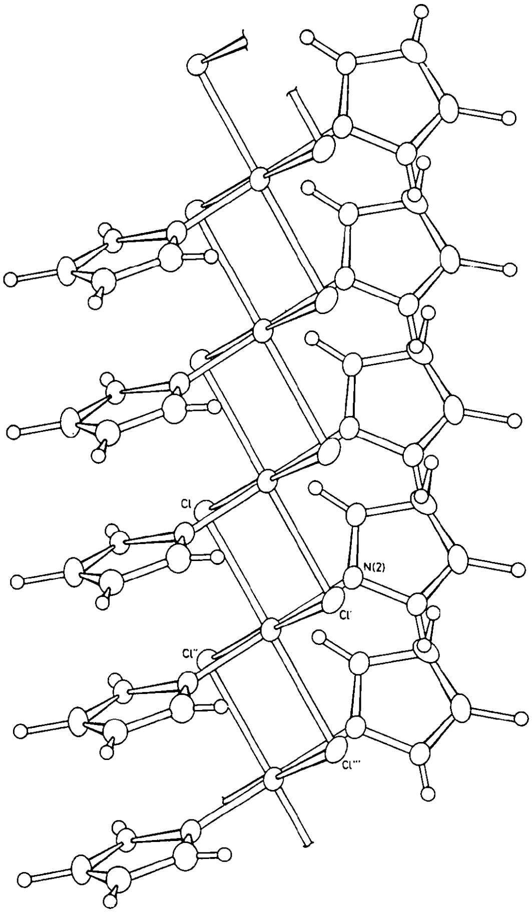

Fig. 3. The arrangement of the atoms in a chain of $Mn(pz)_2Cl_2$ units.

Table 8. *Comparison of mean bond lengths* (Å) *and bond angles* (°) *in pyrazole compounds*

| Distance or angle | $Mn(pz)_2Cl_2^a$ | $Mn(mpz)_4Br_2^b$ | Pyrazole$^c$ | $Ni(pz)_4Cl_2^d$ | $Ni(pz)_6(NO_3)^e$ | $Co[HB(pz_3)]_2^f$ |
|---|---|---|---|---|---|---|
| N(1)–N(2) | 1·337 (4) | 1·351 (3) | 1·352 (3) | 1·344 (4) | 1·354 (3) | 1·364 (6) |
| N(2)–C(3) | 1·334 (4) | 1·320 (3) | 1·328 (10) | 1·325 (3) | 1·332 (6) | 1·330 (6) |
| C(3)–C(4) | 1·395 (5) | 1·388 (4) | 1·389 (13) | 1·391 (4) | 1·381 (5) | 1·393 (7) |
| C(4)–C(5) | 1·342 (5) | 1·356 (5) | 1·371 (15) | 1·364 (5) | 1·357 (7) | 1·379 (7) |
| C(5)–N(1) | 1·339 (4) | 1·332 (3) | 1·337 (5) | 1·345 (4) | 1·344 (5) | 1·339 (6) |
| C(5)–N(1)–N(2) | 111·8 (5) | 113·4 (2) | 113·0 (5) | 111·4 (3) | 111·4 (3) | 109·9 (4) |
| N(1)–N(2)–C(3) | 104·6 (4) | 103·6 (2) | 103·7 (5) | 105·5 (2) | 104·6 (3) | 106·0 (4) |
| N(2)–C(3)–C(4) | 110·9 (5) | 111·4 (2) | 111·8 (6) | 110·6 (3) | 111·3 (4) | 111·2 (5) |
| C(3)–C(4)–C(5) | 104·9 (5) | 106·0 (3) | 105·1 (7) | 105·3 (2) | 105·5 (4) | 104·1 (5) |
| C(4)–C(5)–N(1) | 107·9 (5) | 105·6 (2) | 106·3 (7) | 107·0 (3) | 107·2 (3) | 109·0 (5) |

References: (*a*) Present work(*b*) Reedijk, Stork-Blaisse & Verschoor (1971). (*c*) LaCour & Rasmussen (1973). Because of the high thermal parameters at room temperature the low-temperature values have been taken. (*d*) Reimann, Mighell & Mauer (1967). (*e*) Reimann, Santoro & Mighell (1970). (*f*) Churchill, Gold & Maw (1970).

Table 9. *Comparison of the* H···Cl, N···Cl *distances and* N-H···Cl *angles with literature data*

| | H···Cl$^-$ | N···Cl | ∠N–H···Cl |
|---|---|---|---|
| Hamilton & Ibers (mean values) | 2·45 Å | 3·33 Å | 149° |
| N(1)–H(1)···Cl$^{iii}$ | 2·70 | 3·286 | 130 |
| N(1)–H(1)···Cl$^{iv}$ | 2·84 | 3·527 | 125 |

of distances and angles differ considerably from the mean values of Hamilton & Ibers.

Our arguments are:

(1) The pyrazole ring would be expected to lie perpendicular to the Mn–Mn axis. Such an arrangement minimizes and balances the non-bonded repulsions on H(1) and H(3) and allows maximum overlap of the $\pi$-orbital on N(2) with the $d_{xy}$ orbital of Mn. However, the pyrazole ring is twisted by 26·1°.

(2) The angle between the Mn–N(2) bond and the Cl–Mn–Cl′ plane is distorted from 90° to 87·9°. This again diminishes the overlap of the orbitals on N(2) and Mn.

(3) The non-collinearity of the bonds Mn–N(2) and Mn–N(2′) (178·5°) is again unfavourable to a strong overlap of the orbitals on N(2) and Mn.

(4) The angle Mn–N(2)–N(1) (122·9°) is considerably smaller than the angle Mn–N(2)–C(3) (132·4°, see Fig. 1).

Shorter H···Cl$^-$ (and N···Cl$^-$) distances can only be achieved by heavier distortions. Twisting the pyrazole ring more than 26·1° will be resisted by the van der Waals contacts between adjacent rings in the direction $y$ (by twisting the ring 26·1° the separation diminishes from 3·76 to 3·38 Å), the non-bonded collision between H(3) and Cl (distance 3·02 Å) and by a still smaller overlap of the orbitals on N(2) and Mn.

Further distortion of the Cl–Mn–N(2) and Mn–N(2)–N(1) angles and of the collinearity of the Mn–N(2) and Mn–N(2′) bonds is also resisted by the latter effect. As the same N–H is involved in both hydrogen bonds, it is not possible to obtain higher values for the N–H···Cl angles without a severe distortion of the whole structure.

Evidence for hydrogen bonding was also found in the comparison of the infrared spectra of free gaseous pyrazole (Zecchina, Cerruti, Coluccia & Borello, 1967) and the present compound (Reedijk, 1973). The values obtained for the N–H stretch vibrations are 3541 and 3220 cm$^{-1}$ respectively.

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All crystallographic calculations were carried out on the Leiden University IBM 360/65 computer.

## References

Churchill, M. R., Gold, K. & Maw, C. E. (1970). *Inorg. Chem.* **9**, 1597–1604.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Graaff, R. A. G. de (1973). *Acta Cryst.* A**29**, 298–301.

Hamilton, W. C. & Ibers, J. A. (1968). *Hydrogen Bonding in Solids*. New York, Amsterdam: W. A. Benjamin.

*International Tables for X-ray Crystallography* (1965). Vol. I. Birmingham: Kynoch Press.

La Cour, T. & Rasmussen, S. E. (1973). *Acta Chem. Scand.* **27**, 1845–1854.

Reedijk, J. (1970). *Rec. Trav. Chim. Pays-Bas*, **89**, 605–618.

Reedijk, J. (1973). Private communication.

Reedijk, J., Stork-Blaisse, B. A. & Verschoor, G. C. (1971). *Inorg. Chem.* **10**, 2594–2599.

Reimann, C. W., Mighell, A. D. & Mauer, F. A. (1967). *Acta Cryst.* **23**, 135–141.

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

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Witteveen, H. T. & Reedijk, J. (1973). *Solid State Commun.* **12**, 557–559.

Zecchina, A., Cerruti, L., Coluccia, S. & Borello, E. (1967). *J. Chem. Soc.* (*B*), pp. 1363–1368.