different. O(1) is surrounded by two oxygen and two bromine atoms in approximately tetrahedral coordination at hydrogen-bond distances, whereas O(2) has a pyramidal environment. Both this fact and the short O···O distances indicate that the proton originating from HBr is located somewhere in the O(2)···O(2) bond, and that O(1) is the oxygen of a normal water molecule.

For the space group chosen here, the shortest O···O hydrogen bond is formed between two oxygen atoms across a twofold axis. However, it is not possible to decide from the present investigation whether this bond should be considered symmetric or asymmetric. Corresponding bonds found in similar structures are in the range 2·41–2·43 Å (Lundgren & Olovsson, 1967a,b; Olovsson, 1968). In nitranilic acid hexahydrate (Krogh Andersen, 1967) where the ion $H_5O_2^+$ was also found, the O···O distance is 2·443 Å. The short bond is here not symmetrical according to the space group symmetry. A neutron diffraction study of the compound has shown that the hydrogen atom occupies a slightly asymmetric position, about 0·05 Å from the middle of the bond (Williams, 1969).

The bond distances and angles around O(2) favour the interpretation $H_5O_2^+$ for the grouping O(2)···O(2) rather than $H_3O^+ . H_2O$. The most appropriate formulation of the compound is thus $H_5O_2^+ Br^- . H_2O$. The configuration of the $H_5O_2^+$ ion is *trans*. The situation is analogous to that in the trihydrate of hydrogen chloride (Lundgren & Olovsson, 1967b), where similar considerations give the formulation $H_5O_2^+ Cl^- . H_2O$. However, the two compounds are not isostructural.

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The Crystal and Molecular Structure of (C5H5)2Cr2(NO)3(NH2)

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Crystals of $(C_5H_5)_2Cr_2(NO)_3(NH_2)$ are orthorhombic, space group *Pnma*, with cell dimensions $a = 7·948$ (4), $b = 9·248$ (4), $c = 17·489$ (6) Å, $Z = 4$. Atomic parameters have been determined from three-dimensional scintillation-counter data and refined using full-matrix least-squares methods. The final discrepancy index $R = 0·069$ for the 511 observed reflexions. The chromium atoms are linked together by a chromium–chromium bond [2·650 (4) Å] and by bridging nitrosyl and amido groups. There is a *trans* arrangement of cyclopentadiene and terminal nitrosyl groups. The molecule as a whole achieves mirror symmetry (with disorder of the two bridging groups).

Introduction

A variety of binuclear chromium compounds in which the metal atoms are bridged by nitrogen-containing ligands (NO, NMe₂) are known (Ahmed, Bruce & Knox, 1966). Recently the title compound was pre-

pared (Flitcroft, 1968) and considerable interest was centred in the unusual mixed amido and nitrosyl bridge.

Kettle (1965) has noted that when carbon monoxide molecules are coordinated to metals there is a transfer of electrons from the metal d orbitals to the π^* carbonyl

orbitals. As a result M–C–O fragments may be bent, the extent of the bending being dependent on the difference in occupation of the two π^* orbitals. (The same arguments apply for nitrosyl complexes.) These features coupled with the small size and relative simplicity of the molecule made it an attractive subject for a crystal-structure study.

Crystallographic data

A sample of the compound was kindly provided by Dr N. Flitcroft. No difficulty was encountered in finding suitable crystals. The space group and initial cell dimensions were determined by precession (Mo $K\alpha$) and Weissenberg photographs (Cr $K\alpha$) of the $hk0$, $h0l$ and $0kl–4kl$ zones respectively. More accurate cell dimensions were later obtained from least-squares refinement of 29 general reflexions whose 2θ values were accurately determined, on a Picker 4-circle diffractometer. The crystal data are given in Table 1.

The shape of the crystal could best be described as an irregular rectangular parallelepiped with some truncated corners; the maximum dimensions in the direc-

tions **a**, **b**, and **c** respectively are $0.17 \times 0.36 \times 0.14$ mm. All data were collected with the a axis parallel to φ.

Intensities were measured on a manual diffractometer, equipped with our own semi-automation, using Nb-filtered Mo $K\alpha$ radiation with pulse-height analysis. Each intensity was measured over a 2θ range of $2°$ using $\theta–2\theta$ scan with a take-off angle of $1.3°$. The background was determined by two stationary counts (each for half the scan period) at the limits of the scan. All reflexions with $\sin\theta/\lambda < 0.538$ were measured, of which 511 were accepted as observed. (These reflexions were those that were at least 1.8σ above background.) Standard reflexions were measured every 4 hours and showed no significant change during the entire data collection; the extreme variation of the scale was 3.0%. Lorentz–polarization corrections were made and the intensity data were processed to yield $F(\text{rel})$ in the normal way; (no absorption corrections were made).

Structure analysis

An examination of the intensity data revealed that they could be divided into two parts. The $h+k$ even re-

Table 1. Crystal data

Formula weight $(C_5H_5)_2Cr_2(NO)_3NH_2 = 340.2$

a	7.948 (4) Å
b	9.248 (4)
c	17.489 (6)

Orthorhombic space group $Pnma$ Temperature 21 °C

D_m 1.75 g.cm^{-3} $Z = 4$ D_c 1.69 g.cm^{-3}

$\mu_{\text{Mo }K\alpha}$ 17.6 cm^{-1} (values in parentheses are the standard errors, σ)

Table 2. Atomic coordinates and thermal parameters

	x	y	z	B
Cr(1)	−0.2774 (4)	0.2500	0.0774 (2)	3.24 (8) Å^2
Cr(2)	−0.2334 (4)	0.2500	−0.0728 (2)	3.04 (8)
O(1)	−0.6255 (23)	0.2500	0.1073 (17)	
O(2)	0.1286 (20)	0.2500	−0.0766 (16)	
O(3)	−0.3144 (22)	0.5172 (23)	−0.0011 (13)	4.8 (4)
N(1)	−0.4818 (28)	0.2500	0.0892 (11)	5.1 (4)
N(2)	−0.0232 (28)	0.2500	0.0698 (12)	5.6 (5)
N(3)	−0.2712 (17)	0.4019 (11)	0.0014 (8)	4.2 (2)
C(1)	−0.2060 (82)	0.2500	0.2052 (32)	5.6 (14)
C(2)	−0.1610 (37)	0.3896 (35)	0.1687 (16)	2.3 (5)
C(3)	−0.0188 (25)	0.3340 (27)	0.1183 (11)	1.1 (3)
C(01)	−0.0090 (103)	0.2500	0.1142 (42)	7.9 (19)
C(02)	−0.0978 (52)	0.3581 (48)	0.1503 (22)	4.4 (10)
C(03)	−0.2423 (48)	0.3149 (61)	0.1963 (21)	4.0 (8)
C(4)	−0.2281 (66)	0.2500	−0.1988 (27)	3.7 (10)
C(5)	−0.3313 (55)	0.3581 (46)	−0.1767 (22)	4.2 (9)
C(6)	−0.4674 (43)	0.3259 (42)	−0.1373 (18)	2.7 (7)
C(04)	−0.4852 (49)	0.2500	−0.1277 (22)	2.2 (8)
C(05)	−0.3916 (59)	0.3878 (54)	−0.1546 (25)	6.3 (11)
C(06)	−0.2552 (54)	0.3356 (60)	−0.1907 (22)	4.5 (9)

Anisotropic thermal parameters for O(1) and O(2).

(β_{ij} are the coefficients in the expressions: $\exp[(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$).

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{33}
O(1)	0.0118 (17)	0.0841 (140)	0.0077 (30)	0.0	0.0009 (20)	0.0
O(2)	0.0121 (16)	0.0493 (65)	0.0075 (27)	0.0	0.0018 (20)	0.0

flexions were, in general, much more intense than the $h+k$ odd. Phases were calculated for the more intense data using the Ahmed & Hall (1968) symbolic addition programs.

An approximate structure was derived for this strong subset of the data. However, in spite of the good agreement ($R=0.21$), and chemical reasonableness, it was not found possible to destroy the pseudo-symmetry. It should also be mentioned that amongst the $hk0$ zone only 6 reflexions were observed for $h+k=2n+1$, and these were weak; this indicated an approximate n-glide plane normal to **c**. (This was more strongly indicated than the general c centring.)

Because of our confidence in the phases of the data based on the significant chromium atom contributions, we decided to proceed by applying direct methods to the remaining unknown phases. We selected 39 large reflexions and were able to assign 29 phases of which all proved subsequently to be correct. A three-dimensional Fourier synthesis using these 29 additional reflexions proved sufficient to indicate in which way the structure was distorted from the c-centred lattice.

Considerable difficulty was found in describing the cyclopentadienyl rings. The best description we have been able to make consists of two equal occupancy alternative orientations for each ring, these orientations not having any crystallographic relationship. (This point becomes crucial when the rejection of a centro-symmetric space group is to be considered.)

Refinement of this structure by full-matrix least-squares (using unit weights) proceeded routinely until $R=0.12$ and then stopped. A three-dimensional electron density difference map revealed that the largest features were associated with the two chromium atoms and with the two terminal nitrosyl oxygen atoms. It was found that the two chromium atoms had refined to

coordinates which had x values of -0.264 and -0.220. The electron density difference map suggested the values of -0.27 and -0.24. (Final refined values of -0.2775 and -0.2334 were obtained.) The reason for the failure of the full-matrix refinement to converge was probably due to similarity of the two Cr atoms (see Table 2) whose coordinates could be approximately described as x, y, z and $-\frac{1}{2}-x$, y, $-z$. Furthermore the initial parameters chosen required the path of refinement to cross from one side of these pseudo-equivalent positions to the other. The new positions improved the consistency of the distances between the Cr atoms and the light atoms considerably. It should be noted that there were a large number of severe interactions (correlation coefficients >0.40) amongst the coordinate parameters since the coordinates of one 'half' of the molecule were *approximately* related to those of the other half by a twofold axis. (The positions x, y, z and $-\frac{1}{2}-x$, y, $-z$ are, in general, nearly equivalent.) It was found useful to carry out several cycles refining non-interacting parameters in various combinations before the final two cycles of full-matrix refinement. (Partial shifts would probably have accomplished the same result.) It should be noted that the pseudo-symmetry found at the time of structure solution, by the near (but not exact) c centring, provided a warning of these interactions in an equivalent manner to the coincidences in the Patterson function mentioned by Geller (1961).

After corrections of the chromium atom coordinates the terminal nitrosyl oxygen atoms were permitted anisotropic motion, refinement proceeded and a final residual (R) of 0.069 was obtained. A three-dimensional electron density difference map revealed no features greater than 0.5 e.Å^{-3}. This model of the structure is not altogether a happy one; we did not consider it
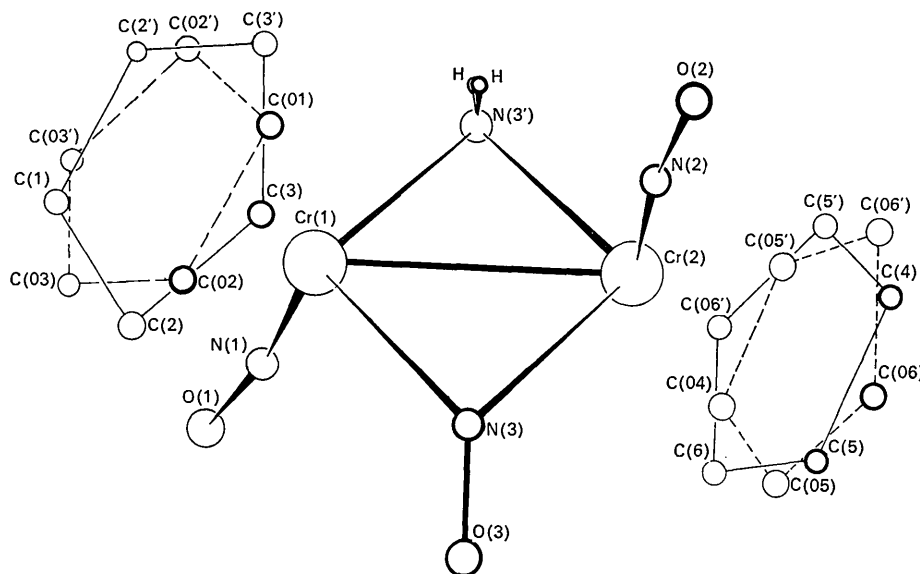

Fig. 1. Molecular structure of $(C_5H_5)_2Cr_2(NO)_3(NH_2)$.

worth while to test a non-centrosymmetric model since the interactions encountered (see Table 3) in this model were quite severe. Moreover, in a model involving almost double the number of parameters any indeterminacy may be expected to be correspondingly worse. This fact coupled with the indication that the cyclopentadiene groups would be disordered even in the non-centrosymmetric case rendered it not worth further pursuit (Geller, 1961).

Table 3. *Correlation coefficients* (>0.4) *for interacting pairs of coordinate parameters*

Cr(1)	x	Cr(2)	x	0·46
	z		z	0·42
C(1)	x	C(03)	x	0·45
	z		z	0·55
C(3)	x	C(01)	x	0·44
	z		z	0·43
	y	C(6)	y	0·44
C(4)	z	C(06)	z	0·43

Table 3 (*cont.*)

C(5)	x	C(06)	x	0·40
C(6)	x	C(04)	x	0·42
C(01)	x	C(04)	x	0·45
C(03)	y	C(06)	y	0·69
	z		z	0·43
N(1)	x	N(2)	x	0·40

During refinement the weighting scheme was examined as a function of $\sin\theta$, $|F|$, and the various parity groups of h, k and l. At no time were significant trends in $\sum\omega\,(|F_o|-|F_o|)^2$ found, though a few of the outstandingly strong reflexions showed unexpectedly good agreement in the final analysis.

Results

The final coordinates are listed in Table 2; the molecular configuration and the packing of the molecules in the crystals are shown in Figs. 1 and 2.

Table 4. *Measured and observed structure factors on 5 × absolute scale*

Scattering factors used were those listed in *International Tables for X-ray Crystallography* (1962). The chromium scattering factor (TFD model) includes both the real and imaginary components of the scattering. In the listing of structure factors (Table 4) F_c is given the sign of the real component and the magnitude of the total value.

Discussion

The structure found is novel in that previously no mixed nitrosyl and amido bridges were known. The molecule has imposed on it an overall crystallographic mirror symmetry; it has in addition an approximate (non-crystallographic) twofold axis of symmetry.

Table 5. *Interatomic distances and angles*

(a) Bonded distances

Cr(1)–Cr(2)	2·650 (4) Å
Cr(1)–N(1)	1·637 (23)
Cr(2)–N(2)	1·672 (23)
Cr(1)–N(3)	1·936 (12)
Cr(2)–N(3)	1·936 (12)
Average Cr——C	2·24 (5)
N(1)–O(1)	1·185 (27)
N(2)–O(2)	1·212 (25)
N(3)–O(3)	1·121 (22)
Average C——C	1·43 (11)

(b) Angles

Cr(1)–N(1)–O(1)	171·7 (2·4)°
Cr(2)–N(2)–O(2)	172·6 (2·5)
Cr(1)–N(3)–O(3)	135·1 (1·7)
Cr(2)–N(3)–O(3)	135·4 (1·7)
N(1)–Cr(1)–N(3)	96·4 (0·7)
N(2)–Cr(2)–N(3)	97·7 (0·7)
N(3)–Cr(1)–N(3)	93·1 (0·8)
N(3)–Cr(2)–N(3)	93·1 (0·8)
Cr(1)–N(3)–Cr(2)	86·4 (0·5)

(c) Intermolecular contacts (< 3.25 Å)

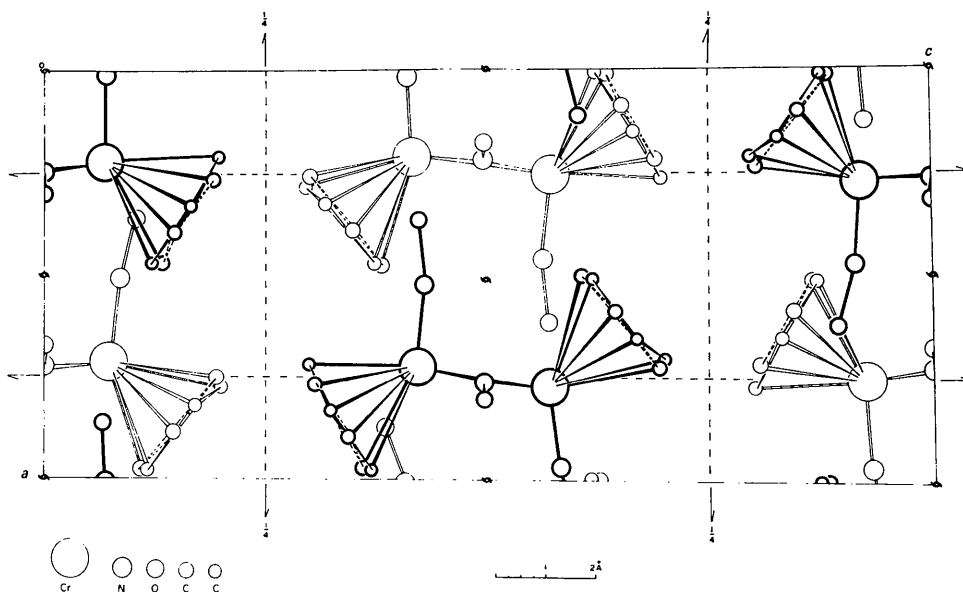|							
O(1)	O(3)	2·88 Å	1	1	$-x$	$1-y$	$-1-z$
	C(3)	3·05	2	2	x	y	$-1+z$
	C(01)	3·23	2	3	$-x$	$1-y$	$-z$
O(2)	O(3)	2·94	3	4	x	y	$1+z$
	C(04)	3·20	4				
O(3)	O(3)	2·97	1				
	N(1)	3·10	1				

Fig. 2. Crystal structure of $(C_5H_5)_2Cr_2(NO)_3(NH_2)$ viewed down the *b* axis.

Because of the crystallographic problems described earlier it has not proved possible to distinguish whether in fact the structure is non-centrosymmetric with no crystallographic molecular mirror plane of symmetry, or alternatively is disordered in the way described.

It has been recognized (Baird, 1968) that both low oxidation states of the metal, and also ligands such as carbonyl or nitrosyl, may help confer stability on metal–metal bonds. Each chromium atom can be regarded as formally zero-valent, and may be regarded as being derived from two $C_5H_5^-$ ions, three NO^+ ions and an NH_2^- ion, the chromium atoms achieving the krypton configuration by the formation of a metal–metal bond.

It has also been recognized (Cotton & Willkinson, 1966) that examination of C–O bond lengths does not provide a fruitful means of assessing the bond order. This is because of the sensitivity of the bond order to small errors in bond length. Since this argument equally applies to nitrosyl compounds it might prove more useful to first examine the Cr–N bond order. The Cr–N–O angles of 171·7 (2·4) and 172·6 (2·5)° (Table 5) indicate that the nitrosyl groups are barely significantly bent.

On the basis of distances in diethylenetriamine-chromium tricarbonyl Cotton & Richardson (1966) have suggested a value of 2·18 Å for the Cr–N single-bond length for formally zero-valent chromium. It has, however, already been questioned by Bush, Sim, Knox, Ahmed & Robertson (1969) whether this value is appropriate and they propose a value of 2·01 Å based on a series of Cr–N distances. In either case the terminal Cr–N (1·63 Å) bonds possess considerable double (and possibly triple) bond character. The terminal N–O bond distances of 1·205 Å (average) are intermediate between the values expected for a double bond and a single bond (in line with the interpretation of the Cr–N distance).

Care must be used in considering the bond order for bridging groups as these distances arise from an imposed geometry. However, the bridging value of 1·93 Å for Cr–N distances is reasonably close to the value proposed by Bush et al. (1969) for single-bond order. The Cr–Cr distance on the other hand is slightly shorter than that found in cis-$[C_2H_5)(NO)Cr(NMe_2)]_2$, 2·72 Å, or in the trans form, 2·67 Å (Table 6). This could be attributed to removal of negative charge from the chromium atom by the additional nitrosyl group. The planes (Table 7) which involve the two bridge bonds to each nitrogen atom are folded about the Cr–Cr bond, these two Cr–N–Cr planes have a dihedral angle of 10·30°. This folding would permit the bending of the Cr–Cr bond to subtend a more satisfactory valence angle with the four Cr-(bridging N) bonds.

The low accuracy of the chromium to cyclopentadiene (cp) carbon atom distances does not warrant discussion but it might be observed that the average value 2·24(5) Å is in the range found for other structures, 2·20–2·26 Å, of similar types (Carter, McPhail & Sim, 1966).

Table 6. Structural data for some metal nitrosyl compounds

Compound	Reference	M–M Å	M–N (terminal) Å	M–N (bridging) Å	N–O Å	M–C* in cp Å	M–N–M °	M–N–O (terminal)
$Cr_2(NO)_3(NH_2)(C_5H_5)_2$	Present paper	2·650 (4)	1·655 (23)*	1·936 (12)	1·198 (23)* bridge / 1·121 (22)	2·24 (5)	8·64 (0·5)	172·2 (2·5)°*
cis-$[C_5H_5Cr(NO)NMe_2]$	Bush et al. (1969)	2·72 (1)	1·63 (1)	2·01 (1)	1·22 (2)	2·26 (1)	85·0 (0·4)	169·1 (0·9)
trans-$[C_5H_5Cr(NO)NMe_2]$	Bush et al. (1969)	2·67 (1)	1·63 (2)	2·00 (1)	1·23 (2)	2·26 (1)	84·3 (0·5)	169·1 (1·3)
$C_5H_5Cr(NO)_2NCO$	Bush et al. (1969)		1·72 (1)		1·16 (1)	2·20 (1)		171·0 (0·6)
$C_5H_5Cr(NO)_2Cl$	Carter et al (1966)		1·710 (13)*		1·140 (19)*	2·199		168·6 (1·3)*
$IrCl(CO)(NO)[P(C_6H_5)_2(BF_4)]$	Hodgson & Ibers (1968)		1·972 (11)		1·16 (1)			124·1 (0·9)
$[Fe(NO)_2SEt]_2$ Roussin's red ester	Thomas et al. (1958)	2·720 (3)	1·671 (15)*		1·171 (22)*			167·4 (3·5)*
$K_3[Mn(NO)(CN)_5]$	Tullberg & Vannerberg (1967)		1·66 (1)		1·21 (2)			174·3 (1·3)

* Denotes average value.

Table 7. *Deviations from mean planes*

' Denotes mirror image.

Equations of planes	Atoms in plane	Atom out of plane	Deviation
$(-0.7884)x+(0.0000)y+(-0.6152)z-(-1.5391)=0$	C(2), C(2'), C(3), C(3')	C(1)	-0.28 (6) Å
$(-0.8188)x+(0.0000)y+(-0.5741)z-(-1.7059)=0$	C(02), C(02'), C(03), C(03')	C(01)	-0.11 (8)
$(-0.8435)x+(0.0000)y+(-0.5371)z-(4.0206)=0$	C(5), C(5'), C(6), C(6')	C(4)	-0.11 (5)
$(-0.8643)x+(0.0000)y+(-0.5030)z-(3.9024)=0$	C(05), C(05'), C(06), C(06')	C(04)	-0.03 (4)
$(-0.1317)x+(-0.0897)y+(-0.9872)z-(1.7916)=0$	Cr(1), Cr(2), N(3)		
$(-0.1317)x+(-0.0897)y+(-0.9872)z-(2.2066)=0$	Cr(1), Cr(2), N(3')		

Wheatley (1967) proposed a Cr–ring (centre) distance of 1·77 Å in unperturbed Cr π-cp complexes. In this case, the average value of the Cr–ring (centre) distance determined is 1·89 Å. This lengthening of the Cr–ring (centre) distance may be due to π back-donation of electrons of the NO group to the metal atom rather than to the electrophilicity of the NO groups proposed by Wheatley (1967).

The two disordered orientations of each cyclopentadiene ring make an angle of less than 3° between themselves. The rings are non-parallel and subtend an angle of at leat 5° (taking the planes nearest parallel in pairs), somewhat higher than the usual maximum of 3°. This may be explained by a combination of the following factors: (i) in the parent molecule, the NO and NH$_2$ groups will not allow mirror symmetry. They provide an asymmetric electronic distribution about the chromium atoms, thus causing a different tilt for each of the cyclopentadiene rings; (ii) disordering of both the cyclopentadiene rings and the parent molecule has the effect of blurring the images of the structure.

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The Crystal Structure of Diethylaminoborondifluoride

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The crystal structure of diethylaminoborondifluoride (C$_2$H$_5$)$_2$NBF$_2$, has been solved, using low-temperature photographic data, and refined to a residual of 11·3% with $\sigma_x \simeq 0.01$ Å. The space group is $P4_2/n$ with $a=b=14\cdot2$, $c=6\cdot44$ Å, $Z=4$ (dimers). The molecule has been confirmed as dimeric with the (B–N)$_2$ ring similar to other (B–N)$_2$ rings but with the B–N bond (1·64 Å) significantly longer.

Introduction

Substituted aminoboranes of the type R$_2$NBX$_2$, where R is methyl or ethyl and X is Cl or F, can exist either as monomers, *e.g.* Et$_2$NBCl$_2$ (Ostoff & Brown, 1952) or as dimers in which (BN)$_2$ forms a four-membered ring as in (Me$_2$NBF$_2$) (Hazell, 1966; Bannister, Greenwood, Straughan & Walker, 1964). Diethylamino-