

Electron Density Distribution in Cyanuric Acid. II.* Neutron Diffraction Study at Liquid Nitrogen Temperature and Comparison of X-ray and Neutron Diffraction Results†

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A low-temperature neutron diffraction analysis of cyanuric acid has been carried out to complement earlier X-ray work. A precision of about 0.001 Å has been achieved in the atomic coordinates. The estimate of the precision is supported by agreement between chemically equivalent bonds. As predicted by earlier infrared data, a small difference (0.01 Å) exists between the two N-H bond lengths, but in contrast to other systems, the shorter N-H bond participates in the shorter hydrogen bond. An analysis of the atomic vibrational parameters clearly shows the presence of N-H stretching and bending vibrations. The X-ray oxygen positions are displaced towards the lone pairs by 0.006 ± 0.001 and 0.003 ± 0.001 Å when compared with the neutron diffraction results. The difference map combining X-ray observations and neutron parameters, shows sharp bonding features in the bonds and in the lone-pair regions. The peaks are higher than those obtained in previous room temperature studies. A refinement on the one-center elements of the first-order density matrix has been completed. It will be described in a subsequent publication.

Introduction

Comparison of X-ray and neutron diffraction studies for a number of small molecules has given evidence for deviations of the atomic charge density from spherical symmetry. These deviations are interpreted as resulting from bonding effects (Coppens, 1967; Coppens, Sabine, Delaplane & Ibers, 1969). The studies indicated that reduction of data collection temperature would be highly desirable for a number of reasons:

(i) The collection of high-order data will lead to an increase of resolution in the electron density maps and allows a more accurate determination of the nuclear positional and temperature parameters with the neutron data.

(ii) A reduction in temperature will reduce the anharmonicity of the molecular vibrations so that introduction of a more complex model in the refinement can be avoided.

(iii) The effect of thermal diffuse scattering (TDS) decreases relative to the intensity of the Bragg reflections when the temperature is lowered, thus reducing one of the sources of error in the temperature parameters.

The present study is a comparative X-ray and neutron diffraction investigation at liquid nitrogen tem-

perature. Cyanuric acid was chosen as the subject of the study, because accurate low temperature X-ray data on this compound had been collected by Verschoor (1964, 1967) and Verschoor & Keulen (1971).

The compound is closely related to *s*-triazine which was studied earlier by a combination of X-ray and neutron diffraction techniques (Coppens, 1967).

Both molecules are planar and have point group symmetry $\bar{6}m2$, but while this symmetry is retained in the crystals of *s*-triazine, in the crystal of cyanuric acid only one twofold axis coincides with a crystallographic symmetry element. Thus chemically equivalent bonds are crystallographically non-equivalent, which provides an internal check on the consistency of the results.

Experimental

(a) Data collection

Neutron intensity data were collected on the Brookhaven Automatic Diffractometer System. The neutron beam was monochromatized by reflection against the (331) plane of a Ge single crystal. This choice completely eliminates second order contamination. The wavelength was measured as 1.067 Å with the aid of a standard KBr crystal.

Crystals were kindly supplied by Dr Verschoor. Two sets of data on different crystals were collected. However, the data collected with the second, larger, crystal were clearly superior as evidenced by good ($R \approx 0.02$) agreement between symmetry-related reflections. Only this second set of data has been utilized in this study.

* Part I: Verschoor & Keulen (1971).

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The crystal had a volume of 2.2 mm³ and was mounted with its *b* axis parallel to the φ axis of the diffractometer. The intensities of 1345 reflections, corresponding to two quadrants of the reciprocal lattice, were recorded at a temperature of approximately 125 °K. Cooling was achieved with the Automatic Low Temperature Apparatus (ALTA) designed and built by Rudman & Godel (1969). This apparatus provides a cold stream of dry nitrogen through a flexible transfer line, which remains pointed at the crystal for all settings of the diffractometer circles.

(b) Choice of temperature

It was considered of importance to match the sample temperature to the temperature at which the X-ray experiment was conducted. The cell parameters given by Verschoor & Keulen (1971) (Table 1) provide an obvious criterion for the temperature as the *a** axis shows a variation of about 2% on cooling. This corresponds to an average variation of 0.0071°/degree C ($\lambda = 1.067 \text{ \AA}$) for 2θ of the strong 600 reflection. The Bragg angle on the diffractometer can be measured within a maximum error of $\pm 0.01^\circ$. The corresponding accuracy of $\pm 1\text{--}2^\circ\text{C}$ was considered sufficient for the experiment.

Table 1. Cell dimensions according to Verschoor & Keulen (1971)

	296 °K	100 °K
<i>a</i>	7.900 (3) Å	7.749 (1) Å
<i>b</i>	6.732 (3)	6.736 (3)
<i>c</i>	11.951 (6)	11.912 (4)
β	130.67 (2)°	130.69 (2)°
Space group	<i>C</i> 2/ <i>n</i>	<i>C</i> 2/ <i>n</i>
<i>Z</i>	4	4

Notwithstanding the care which was taken to ensure temperature matching, the refinement indicated that the X-ray temperature had been appreciably lower, perhaps by as much as 30–40 °C, than the temperature of the present investigation. This would have corresponded to a change of 0.25° in $2\theta_{600}$, which was clearly not observed.

It transpired later that the X-ray cell dimensions were probably determined at a temperature perhaps 10–20 degrees higher than the one at which data were collected (see Verschoor & Keulen, 1971). This explains in part why the temperature of the two experiments was not matched with sufficient accuracy. The consequences of this are discussed in the section on the comparison of the X-ray and neutron diffraction results.

The most likely temperatures of data collection are

now estimated as 85–95 °K and 120–130 °K for the X-ray and the neutron diffraction studies respectively.

Data reduction

An absorption correction ($\mu = 1.72 \text{ cm}^{-1}$) was applied with the program *DATAP7*, which is a generalization of the procedure described by Coppens, Leiserowitz & Rabinovich (1965). The absorption correction was first calculated for a limited number of reflections with several different Gaussian grids to ensure that the grid finally selected produced the required accuracy of better than 1% in the absorption correction.

Symmetry-equivalent reflections were not averaged because a refinement of anisotropic extinction parameters was intended. It has been found that this anisotropy does not always conform to crystal symmetry (Coppens & Hamilton, 1970).

Refinement of the structure

Both neutron and X-ray data were refined with the Brookhaven least-squares program *LINUS*. The X-ray refinement was undertaken because a block-diagonal approximation was used in the initial treatment (Verschoor & Keulen, 1971).

The molecules lie on a twofold axis of the space group *C*2/*n* and one asymmetric unit contains only half a molecule (see Fig. 1 for numbering of the atoms).

(a) Neutron diffraction data

The scattering lengths used for refining the neutron diffraction data were 0.665, 0.94, 0.577 and -0.372 cm^{-12} for C, N, O and H respectively.

The standard deviations of the structure factors were derived from the standard deviations of the intensities in the usual way. The latter were obtained according to the expression: $\sigma^2(I - B) = I + B + \{0.02(I - B)\}^2$ where *I* and *B* are the measured intensity and the background. The value of 0.02 was estimated from the reproducibility of the observations and the agreement between the intensities of symmetry related reflections.

In order to evaluate the importance of extinction in the data an anisotropic extinction refinement (Coppens & Hamilton, 1970) was undertaken. The resulting *R* values (Table 2) for both type I (mosaic-spread dominated) extinction and type II (particle-size dominated) extinction show no improvement over the *R* value obtained with one isotropic extinction parameter. As anisotropic extinction effects were small and changes in

Table 2. *R* values

$$R = \frac{\sum |F_o - |F_c||}{\sum F_o} \quad R_w = \left\{ \frac{\sum w |F_o - |F_c||^2}{\sum w F_o^2} \right\}^{\frac{1}{2}}$$

Neutron data	Isotropic extinction	Type I extinction	Type II extinction	Isotropic extinction and allowing for multiple reflection
<i>R</i>	0.030	0.031	0.030	0.030
<i>R_w</i>	0.030	0.031	0.029	0.027

the parameters on introduction of the anisotropy were everywhere less than one standard deviation, the isotropic treatment was selected.

A number of reflections showed considerably larger than average discrepancies between F_o and F_c after several cycles of refinement. As these discrepancies were thought to be due to multiple reflection effects, the geometrical conditions for multiple reflection were analyzed with the program *MULREF* (Coppens, 1968a). Fifty-eight (out of 1345) reflections, which, according to *MULREF*, could have been affected by multiple reflection were given zero weight in the final refinement. This led to a 10% decrease in R_w (Table 2), while the y coordinates of the atoms C(1), C(2) and O(2) changed by respectively -0.00013 , 0.00013 and 0.00016 . As the b axis is 6.736 Å long these changes are very small. But, they are of the same magnitude as the final estimated standard deviations and the internal consistency attained in the analysis.

Final parameters and their standard deviations are listed in Table 3, while Table 4 contains a list of observed and calculated structure factors and the extinction factors multiplying the intensity of each reflection.

(b) X-ray diffraction data

Verschoor & Keulen's values for the standard deviations of the observations were used without modification. A semi-empirical correction for extinction had been applied to the X-ray data by Verschoor. To provide a further check on this procedure the corrected data were subjected to an isotropic extinction refinement. Extinction in the corrected data was found to be negligible, indicating that the original correction had been quite accurate.

An attempt to consider anisotropic thermal parameters for hydrogen led to unrealistically small vibrations in some directions. Therefore, only the X-ray re-

finements with isotropic thermal parameters for the hydrogen atoms are considered below.

In Table 5, the results of various refinements are compared. Columns 1 and 2 contain the results of the block-diagonal refinement of Verschoor & Keulen and the full-matrix refinement with the same scattering factors [except for using C (ground state) rather than C (valence)] according to analytical expressions given by Moore (1963). Columns 3-7 give the results of several full-matrix refinements with the tabulated values for C

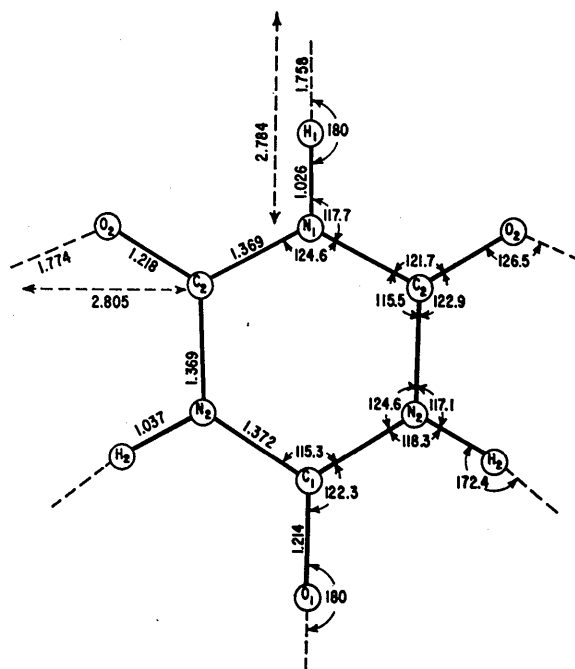


Fig. 1. Bond lengths and angles in cyanuric acid as determined by neutron diffraction. The hydrogen bonds are indicated by dashed lines.

Table 3. Final neutron diffraction parameters

The thermal parameters are in 10^{-4} Å².

The temperature factor used is

$$T(hkl) = \exp \left[-2\pi^2(h^2a^2U_{11} + k^2b^2U_{22} + l^2c^2U_{33} + 2hka*b*U_{12} + 2klb*c*U_{23} + 2hla*c*U_{13}) \right].$$

	x	y	z
C(2)	0.24525 (7)	0.10588 (6)	0.14623 (5)
C(1)	0.25	0.41791 (9)	0.25
N(2)	0.24460 (6)	0.30901 (5)	0.15046 (3)
N(1)	0.25	0.01141 (6)	0.25
O(2)	0.24262 (9)	0.01375 (8)	0.05712 (6)
O(1)	0.25	0.59818 (12)	0.25
H(2)	0.24225 (19)	0.38450 (16)	0.07366 (12)
H(1)	0.25	-0.14096 (21)	0.25

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
C(2)	138 (2)	85 (2)	101 (2)	-3 (2)	-1 (1)	89 (2)
C(1)	162 (3)	71 (3)	135 (3)			112 (2)
N(2)	188 (2)	85 (1)	135 (1)	-3 (1)	5 (1)	125 (1)
N(1)	182 (2)	80 (2)	113 (2)			112 (2)
O(2)	212 (2)	100 (2)	136 (2)	-7 (2)	-10 (2)	141 (2)
O(1)	286 (4)	73 (3)	235 (4)			198 (3)
H(2)	361 (5)	194 (4)	240 (4)	-1 (4)	34 (3)	232 (4)
H(1)	371 (7)	134 (6)	269 (6)			239 (6)

Numbers in parentheses in the Tables are the standard deviations as calculated by the least-squares program.

Table 4. List of observed and calculated structure factors and the extinction correction to the intensities

Table with multiple columns including h, k, l, Fobs, Fcalc, Ext, and various numerical values. The table is organized into sections for different reflections (e.g., h=0, h=1, h=2, h=3) and includes columns for observed (Fobs) and calculated (Fcalc) structure factors, as well as extinction correction (Ext) values. The data is presented in a grid-like format with some rows containing multiple values for the same reflection indices.

Table 4 (cont.)

Table with multiple columns of numerical data, organized into sections with headers like 'K L HIRS FCALC EXT', 'H= 7', and 'H= 8'. The data includes values for various parameters across different rows and columns.

(ground state), N and O as listed in International Tables for X-ray Crystallography (1962) and H as given by Stewart, Davidson & Simpson (1965).

Comparison of the parameters in columns 1-3 shows that the atomic coordinates are not affected much by the change in treatment, but that there are appreciable

Table 5. Parameters obtained from different refinements

Columns 1-7, X-ray (X.R.); Column 8, Neutron diffraction (N.D.); $L = \sin \theta/\lambda$, $L(\max) = 0.8 \text{ \AA}^{-1}$. The U values are in 10^{-4} \AA^2 .

K	x y z	1 X.R.1* 10.00	2 X.R.2* 9.98 (3)	3 Full L 9.99 (3)	4		5		6		7		8 N.D.†
					L > 0.5 9.67 (4)	L > 0.6 10.01 (7)	L < 0.5 10.15 (7)	L < 0.6 10.17 (4)	L < 0.5 10.15 (7)	L < 0.6 10.17 (4)			
C(2)	x	0.24524	0.24524 (13)	0.24521 (13)	0.24517 (12)	0.24505 (12)	0.24525 (25)	0.24529 (18)	0.24525 (7)	0.24529 (18)	0.24525 (7)	0.24525 (7)	
	y	0.10556	0.10555 (9)	0.10559 (10)	0.10558 (9)	0.10565 (8)	0.10591 (25)	0.10562 (16)	0.10588 (6)	0.10562 (16)	0.10588 (6)	0.10588 (6)	
	z	0.14617	0.14618 (8)	0.14617 (8)	0.14618 (8)	0.14618 (8)	0.14621 (17)	0.14621 (17)	0.14612 (11)	0.14623 (5)	0.14612 (11)	0.14623 (5)	
C(1)	y	0.41797	0.41804 (15)	0.41806 (15)	0.41784 (13)	0.41758 (13)	0.41844 (38)	0.41835 (24)	0.41791 (9)	0.41835 (24)	0.41791 (9)	0.41791 (9)	
N(2)	x	0.24447	0.24451 (12)	0.24453 (12)	0.24455 (12)	0.24463 (12)	0.24460 (23)	0.24457 (17)	0.24460 (6)	0.24457 (17)	0.24460 (6)	0.24460 (6)	
	y	0.30893	0.30891 (9)	0.30892 (9)	0.30921 (9)	0.30896 (9)	0.30843 (20)	0.30892 (14)	0.30901 (5)	0.30892 (14)	0.30901 (5)	0.30901 (5)	
	z	0.15034	0.15035 (7)	0.15032 (7)	0.15016 (7)	0.15024 (7)	0.15079 (17)	0.15046 (10)	0.15046 (3)	0.15046 (10)	0.15046 (3)	0.15046 (3)	
N(1)	y	0.01140	0.01139 (13)	0.01140 (13)	0.01089 (14)	0.01105 (13)	0.01266 (36)	0.01187 (21)	0.01141 (6)	0.01187 (21)	0.01141 (6)	0.01141 (6)	
O(2)	x	0.24281	0.24283 (10)	0.24283 (10)	0.24289 (10)	0.24297 (11)	0.24271 (18)	0.24277 (14)	0.24262 (9)	0.24277 (14)	0.24262 (9)	0.24262 (9)	
	y	0.01341	0.01333 (8)	0.01331 (8)	0.01334 (9)	0.01319 (8)	0.01340 (14)	0.01343 (11)	0.01375 (8)	0.01343 (11)	0.01375 (8)	0.01375 (8)	
	z	0.05672	0.05674 (6)	0.05670 (6)	0.05667 (6)	0.05668 (7)	0.05680 (12)	0.05686 (9)	0.05712 (6)	0.05686 (9)	0.05712 (6)	0.05712 (6)	
O(1)	y	0.59856	0.59864 (11)	0.59868 (11)	0.59884 (11)	0.59869 (11)	0.59827 (24)	0.59836 (16)	0.59818 (12)	0.59836 (16)	0.59818 (12)	0.59818 (12)	
H(2)	x	0.2435	0.2415 (19)	0.2416 (19)	0.2458 (26)	0.2445 (39)	0.2408 (24)	0.2407 (22)	0.24225 (19)	0.2407 (22)	0.24225 (19)	0.24225 (19)	
	y	0.3760	0.3717 (19)	0.3706 (19)	0.3624 (26)	0.3723 (42)	0.3663 (30)	0.3702 (23)	0.38450 (16)	0.3702 (23)	0.38450 (16)	0.38450 (16)	
	z	0.0844	0.0836 (13)	0.0846 (13)	0.0943 (19)	0.0913 (30)	0.0867 (19)	0.0846 (15)	0.07366 (12)	0.0846 (15)	0.07366 (12)	0.07366 (12)	
H(1)	y	-0.1222	-0.1124 (31)	-0.1096 (32)	-0.0866 (57)	-0.1096 (187)	-0.1033 (46)	-0.1088 (39)	-0.14096 (21)	-0.1088 (39)	-0.14096 (21)	-0.14096 (21)	

Table 5 (cont.)

	1	2	3	4	5	6	7	8
	X.R.1*	X.R.2*	Full L	L > 0.5	L > 0.6	L < 0.5	L < 0.6	N.D.†
C(2)	U ₁₁	83 (3)	78 (3)	82 (3)	97 (3)	39 (10)	53 (5)	100 (2)
	U ₂₂	76	68 (2)	59 (2)	62 (3)	96 (11)	107 (6)	62 (2)
	U ₃₃	81	80 (3)	67 (3)	78 (2)	87 (10)	86 (5)	73 (2)
	U ₁₂	-3	-3 (2)	-3 (2)	-3 (2)	3 (6)	-1 (4)	-2 (2)
	U ₂₃	5	5 (2)	5 (2)	6 (2)	1 (8)	-0 (1)	-0 (1)
U ₁₃	54	52 (3)	50 (2)	52 (2)	62 (2)	26 (8)	36 (4)	65 (2)
C(1)	U ₁₁	106 (4)	101 (3)	103 (4)	103 (4)	55 (13)	78 (8)	118 (3)
	U ₂₂	68 (4)	65 (4)	54 (3)	54 (3)	114 (16)	94 (7)	51 (3)
	U ₃₃	100 (4)	95 (4)	88 (3)	88 (3)	98 (14)	105 (4)	98 (3)
	U ₁₃	71 (4)	68 (4)	70 (3)	73 (2)	42 (8)	56 (7)	81 (2)
N(2)	U ₁₁	146 (3)	142 (3)	133 (2)	133 (2)	149 (9)	144 (5)	137 (1)
	U ₂₂	60	57 (2)	47 (2)	54 (2)	88 (9)	91 (5)	62 (1)
	U ₃₃	100	94 (3)	86 (2)	95 (2)	92 (10)	106 (5)	99 (1)
	U ₁₂	-1	0 (2)	-2 (2)	-2 (2)	0 (6)	1 (4)	-2 (1)
	U ₂₃	8	10 (2)	4 (2)	4 (2)	26 (7)	19 (4)	4 (1)
	U ₂₃	96	95 (2)	93 (2)	87 (2)	94 (8)	94 (4)	91 (1)
	U ₁₃	138	139 (4)	136 (3)	130 (4)	138 (3)	170 (13)	142 (7)
N(1)	U ₂₂	49	40 (3)	33 (2)	33 (2)	22 (16)	57 (7)	58 (2)
	U ₃₃	86	88 (3)	84 (4)	74 (3)	112 (12)	111 (7)	82 (2)
	U ₁₃	83	85 (3)	84 (3)	79 (3)	105 (10)	89 (6)	82 (2)
	U ₁₁	153	152 (3)	149 (2)	140 (2)	147 (9)	154 (5)	155 (2)
	U ₂₂	84	83 (2)	80 (2)	73 (2)	80 (3)	105 (8)	107 (4)
O(2)	U ₃₃	101	101 (3)	97 (2)	88 (2)	109 (8)	112 (4)	99 (2)
	U ₁₂	-7	-7 (2)	-7 (2)	-6 (2)	-9 (4)	-9 (3)	-5 (3)
	U ₂₃	-11	-12 (2)	-11 (2)	-12 (1)	-17 (5)	-14 (3)	-7 (2)
	U ₂₃	99	99 (2)	97 (1)	90 (2)	95 (7)	101 (4)	103 (2)
	U ₁₃	200	199 (4)	194 (3)	187 (3)	206 (2)	207 (11)	206 (7)
O(1)	U ₂₂	56	56 (3)	53 (3)	40 (3)	54 (14)	70 (6)	54 (3)
	U ₃₃	174	172 (4)	169 (4)	165 (3)	185 (10)	187 (6)	171 (4)
	U ₁₃	134	137 (4)	134 (4)	131 (3)	142 (8)	143 (6)	145 (4)
H(2)	B	1.0	1.2 (0.2)	1.2 (0.2)	0.5 (0.2)	0.7 (0.4)	1.2 (0.3)	
H(1)	B	1.5	1.8 (0.3)	1.7 (0.4)	1.1 (0.4)	-0.2 (0.6)	1.2 (0.4)	
Number observations		967	967	724	537	244	430	
Number variables		49	49	49	49	49	49	
R		0.041	0.041	0.042	0.040	0.027	0.030	
R _w		0.034	0.033	0.026	0.021	0.028	0.031	

* $f(H) = f(\text{Stewart})$ in all X-ray refinements.1: f according to Moore (1963), $f(C) = C(\text{valence})$, least-squares block-diagonal.2: f according to Moore (1963), $f(C) = C(\text{ground})$, full-matrix.3 to 7: f International Tables, $f(C) = C(\text{ground})$, full-matrix.† Neutron diffraction U_{ij} values multiplied by 0.728. See text.

changes in the thermal parameters. This emphasizes the importance of the use of full-matrix least-squares programs and reliable scattering factors in accurate crystallographic work.

The refinements with limited sets of data, the results of which are listed in columns 4 through 7 of Table 5 are of special importance for comparison with the neutron diffraction results, because the high order intensities are to a large extent determined by the core-electron distribution, while the relative contribution of the valence electrons (1 shell, $n=2$) is much more important for the low-order reflections. The details of these refinements and their comparison with the neutron diffraction results (listed in the last column of Table 5) will be analyzed below in a separate section.

Discussion of the neutron diffraction results

(a) Molecular dimensions

The molecular dimensions obtained in this study (Fig. 1, Table 6) are very similar to the results of Verschoor & Keulen (1971), who found good agreement with other heterocyclic molecules. Nevertheless, some small systematic differences are obtained in the oxygen atom positions, which will be discussed later in this article.

Table 6. Atomic distances and angles of the X-ray and neutron diffraction studies*

For numbering of atoms, see Fig. 1, for numbering of molecules see Verschoor & Keulen (1971), Fig. 10.

	X.R.†	N.D.
C(1)---O(1)	1.2161 (14) Å	1.2143 (11) Å
C(2)---O(2)	1.2236 (10)	1.2183 (7)
C(1)---N(2)	1.3729 (9)	1.3715 (6)
C(2)---N(2)	1.3708 (10)	1.3694 (8)
C(2)---N(1)	1.3683 (9)	1.3692 (6)
N(1)---H(1)	0.790 (25)	1.0264 (15)
N(2)---H(2)	0.873 (14)	1.0365 (11)
O(1)-----(H)-N ^{III} (1)	2.7812 (17)	2.7835 (15)
O(2)-----(H)-N ^{III} (2)	2.8006 (12)	2.8051 (10)
O ^{III} (2)---C ^V (2)	2.9777 (13)	2.9780 (11)
H ^{III} (1)---H ^{VI} (2)	3.047 (12)	3.0242 (14)
O ^{III} (2)---O ^{VI} (1)	3.0459 (11)	3.0465 (11)
O ^{III} (2)---C ^{VI} (1)	3.0592 (11)	3.0618 (11)
O ^{III} (2)---O ^V (2)	3.0649 (14)	3.0582 (13)
O(2)---C(2)---N(1)	121.92 (7)°	121.68 (5)°
O(2)---C(2)---N(2)	122.76 (7)	122.87 (5)
N(1)---C(2)---N(2)	115.32 (7)	115.45 (4)
O(1)---C(1)---N(2)	122.41 (5)	122.33 (3)
N(2)---C(1)---N(1)	115.19 (10)	115.33 (6)
H(2)---N(2)---C(2)	116.1 (7)	117.14 (7)
H(2)---N(2)---C(1)	119.2 (7)	118.28 (8)
C(2)---N(2)---C(1)	124.66 (8)	124.57 (4)
H(1)---N(1)---C(1)	117.57 (5)	117.69 (3)
C(2)---N(1)---C(2)	124.86 (9)	124.61 (6)
C(2)---O(2)---H ^{III} (2)	125.5 (3)	126.52 (7)
C(1)---O(1)---H ^{II} (1)	180	180
O(2)---H ^{III} (2)---N ^{III} (2)	174.4 (10)	172.44 (10)
O(1)---H ^{II} (1)---N ^{II} (1)	180	180

* All intermolecular distances shorter than 3.10 Å are listed. No corrections for libration were applied.

† Based on the coordinates of Table 5, column 3.

(b) Hydrogen bonding

N-H---O bond lengths reported in literature are in the range 2.80 to 3.30 Å [for a survey see Hamilton & Ibers (1968)]. The two hydrogen bonds in cyanuric acid are at the lower end of this range (2.8051 ± 0.0010 and 2.7835 ± 0.0015 Å) and can therefore be considered strong N-H---O hydrogen bonds. It was concluded earlier on the basis of single-crystal infrared measurements (Newman & Badger, 1952) that the two bonds are different. The difference between the N-H bond lengths is 0.01 Å, which is small but significant at the level of accuracy attained. As expected, the larger N-H stretching frequency corresponds with the shorter N-H bond length (see summary of frequencies and geometrical parameters in Table 7). But contrary to what is found in many other systems, the shorter N-H bond participates in the shorter rather than in the longer hydrogen bond. This indicates that the strength of the O---H interaction is not only dependent on O---H distance, and leads to the conclusion that the complete linearity of the N(1)-H(1)---O'(1)-C'(1) system is somewhat less favorable for the attraction between N-H and O=C than the more commonly observed geometry in which the angle at the oxygen atom is close to 120°. The explanation lies undoubtedly in the directional character of the lone-pair hybrid orbitals on the oxygen atoms.

Table 7. Hydrogen bonding in cyanuric acid

	N(1)-H(1)---O(1)	N(2)-H(2)---O(2)
$\nu_{\text{N-H}}$	3210 cm ⁻¹	3060 cm ⁻¹
N-H---O	2.7835 (15) Å	2.8051 (10) Å
N-H	1.0264 (15)	1.0365 (11)
H---O	1.7571 (15)	1.7744 (12)
∠N-H---O	180°	172.44 (10)°
∠H---O-C	180	126.52 (7)

(c) Thermal motion

The rigid-body analysis of the X-ray data showed large significant differences between some of the observed and calculated U_{ij} vibration parameters (Verschoor & Keulen, 1970). The discrepancies can be due to internal modes of the molecule or to the influence of bonding effects on the X-ray thermal parameters (Coppens, 1968b). As bonding does not affect the neutron parameters, the ambiguity can now be resolved.

The first rigid-body analysis, in which the elements of the \mathbf{T} and $\mathbf{\omega}$ tensors and the position of the center of libration (Hirshfeld & Rabinovich, 1966) were varied using all atomic vibrational parameters, showed large excess motion of the hydrogen atoms. Since this excess motion is undoubtedly due to N-H stretching and bending modes, zero weights were assigned to the hydrogen-atom parameters. The results given in Tables 8 and 9 indicate that internal modes in the heterocyclic ring cannot be neglected. It appears that in the direction perpendicular to the molecular plane, the carbon atoms vibrate less and the nitrogen atoms more than calculated from the rigid-body parameters, while the agree-

ment for the oxygen atoms is very close. The effect is the same as observed in the X-ray study and apparently represents a puckering mode of the aromatic ring.

Table 8. *Principal axes of T and ω tensors*

α , β and γ are the angles of the main axes with a^* , b^* and c^* respectively, T_{ii} is in 10^{-4} \AA^2 and ω_{ii} in 10^{-4} rad^2 .

	α	β	γ	Magnitude
T_{11}	0.0°	90°	49.3	142
T_{22}	90.1	90	139.5	80
T_{33}	90	0	90	74
ω_{11}	76.5	90	125.8	14
ω_{22}	90	0	90	11
ω_{33}	13.6	90	35.8	6

Coordinate of center of libration: $y = 0.1236$

Coordinate of center of gravity: $y = 0.2094$

The N-H internal vibrations, which were studied by infrared spectroscopy by Newman & Badger (1952), are

evident from the comparison of observed and calculated vibrational parameters (Table 10). The hydrogen atoms undergo motion in excess to the rigid-body vibrations for the direction along the N-H bond and two directions perpendicular to the bond. Calculations with the harmonic-oscillator model show that the displacements are almost totally due to zero-point motion. Corresponding frequencies are given in the third column of Table 10. The agreement with the infrared frequencies (column four) is fair, probably as good as can be expected in view of the experimental errors and the approximations of the rigid-body and harmonic-oscillator models.

It is worthwhile noting that internal vibrations will become increasingly evident as the temperature is lowered. They are high-frequency modes with an appreciable temperature independent zero-point component. On the other hand, the displacement due to the low-frequency rigid-body modes decreases with temperature down to the liquid helium region (see Fig. 2).

Table 9. *Observed and calculated vibration components ($\text{\AA}^2 \times 10^4$) in molecular coordinate system*

Axis 1 is along the twofold axis; axis 2 is perpendicular to the twofold axis in the molecular plane; Axis 3 is perpendicular to the molecular plane.

		C(2)	C(1)	N(2)	N(1)	O(2)	O(1)	H(2)	H(1)
U_{11}	obs	85	71	85	80	100	73	194	134
	calc	84	74	83	74	109	74	103	74
U_{22}	obs	74	102	91	75	74	170	158	200
	calc	80	107	90	84	83	150	101	102
U_{33}	obs	138	162	188	183	212	285	361	372
	calc	158	196	178	150	205	283	231	186
U_{12}	obs	1	0	9	0	-7	0	45	0
	calc	-1	0	10	0	-12	0	25	0
U_{23}	obs	-1	-9	-5	6	-7	-18	0	1
	calc	-1	-9	-4	-2	-2	-21	-7	-7
U_{13}	obs	3	0	3	0	7	0	2	0
	calc	0	0	-3	0	3	0	-7	0

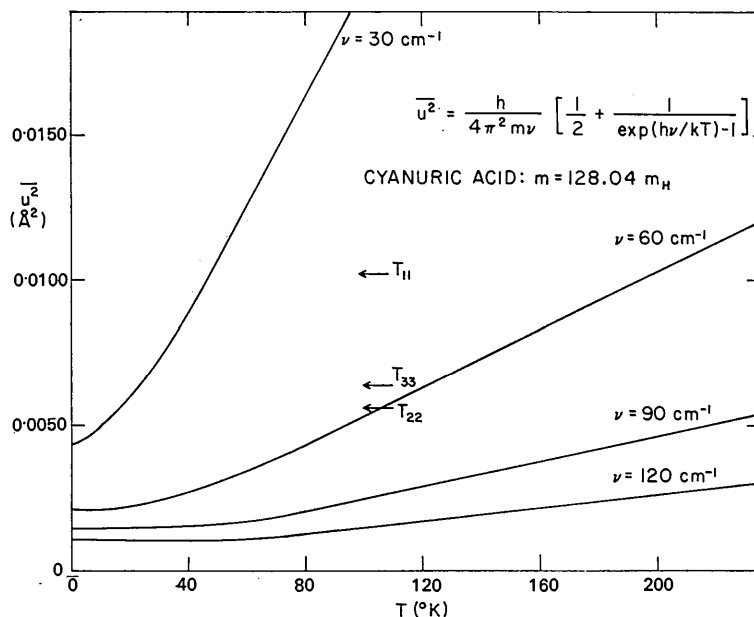


Fig. 2. Mean-square displacement against temperature for a number of frequencies for a vibrator with the mass of the cyanuric acid molecule. Arrows indicate rigid body translational amplitudes as determined with the X-ray data.

The position of the center of libration is displaced towards N(1) by 0.57 Å with respect to the molecular center of gravity. The corresponding number in the X-ray analysis, arrived at by trial and error, rather than by least squares, was 0.5 Å, an exceedingly good agreement.

A TLS analysis according to Schomaker & Trueblood (1968) showed that the elements of the S tensor are small compared with their standard deviations, the only element that is significantly different from zero is four times its standard deviation. This indicates that the approximation of the intersecting libration axes is reasonable for the molecules of cyanuric acid.

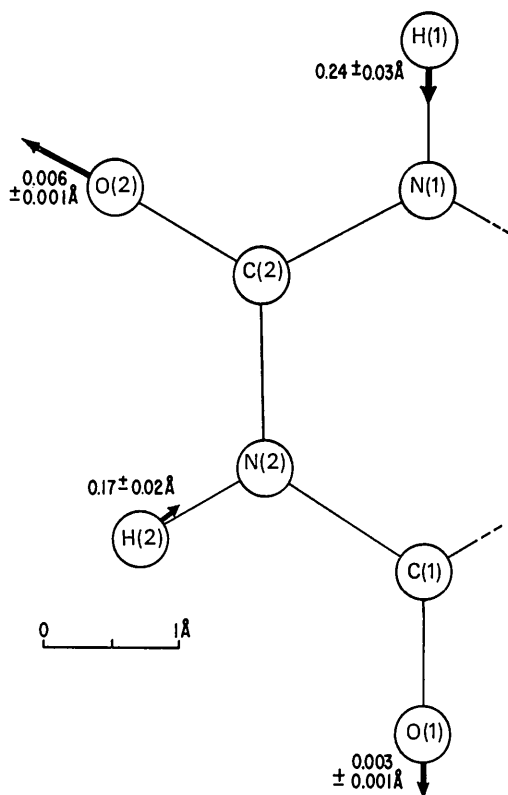


Fig. 3. Difference between X-ray and neutron atomic positions. The apparent shifts of the atoms as located with X-rays are indicated by arrows. The size of the arrows for the O atoms has been magnified by a factor 100. Shifts for C and N atoms are not significant and have been omitted.

Finally, a higher cumulant analysis (Johnson, 1969) of the data, performed by C. K. Johnson (private communication), produced only a marginally significant improvement of 6% of the original value of the *R* value on the introduction of 56 additional parameters. Apparently, the harmonic model with second cumulants only, provides a proper description of the motion of the cyanuric acid molecule at low temperature.

Comparison of the X-ray and neutron diffraction results

(a) Atomic coordinates

Small but significant differences are observed between the X-ray and neutron diffraction results. They are demonstrated in Fig. 3 which shows the positions of the atoms projected onto the plane $x=0.25$ (this is approximately the plane of the molecule). Similar systematic discrepancies have been found in *s*-triazine (Coppens, 1967), hexamethylenetetramine (Duckworth, Willis & Pawley, 1969) and α -proto-oxalic acid and α -deutero-oxalic acid (Coppens, Sabine, Delaplane & Ibers, 1969). This last paper contains a summary of the size and the direction of the shifts which are attributed to the non-coincidence of the centroid of the atomic charge distribution and the nucleus (Coppens & Coulson, 1967).

In cyanuric acid the X-ray positions for O(1) and O(2) are displaced with respect to the nuclear positions towards the lone pairs, by 0.003 (1) and 0.006 (1) Å respectively. It is noteworthy that for both atoms the positions obtained from the low order refinement (Table 5) are closer to the neutron diffraction positions than those of the high-order and full refinements. For example, the shift of 0.006 Å for O(2) is reduced to 0.004 Å (which is no longer significant) for the refinements in which only data with $\sin \theta/\lambda < 0.5 \text{ \AA}^{-1}$ or $\sin \theta/\lambda < 0.6 \text{ \AA}^{-1}$ were included, while the corresponding numbers for O(1) are 0.003 and 0.001 Å.

Earlier model calculations have shown that beyond $\sin \theta/\lambda = 0.5 \text{ \AA}^{-1}$ the scattering by bond density becomes small in comparison with the effect of the asphericity caused by the lone-pair electrons (Dawson, 1964; Coppens, 1969). The relative shifts of the oxygen atoms in cyanuric acid can be interpreted on this basis. It appears that in the low-order refinement the lone-pair electrons and the overlap density in the C=O bond al-

Table 10. Comparison of neutron diffraction and infrared evidence on N-H internal vibrations

	Root-mean-square displacement	Corresponding frequency	Infrared frequency (Newman & Badger, 1952)
N(1)-H(1) stretching	0.078 Å	2790 cm^{-1}	3210 cm^{-1}
in plane bending	0.099	1710	1410-1425
out of plane bending	0.136	850	807 (?)
N(2)-H(2) stretching	0.075	2930	3060
in plane bending	0.096	1740	1410-1425
out of plane bending	0.113	1290	807 (?)

most balance each other, while at higher angles the effect of the lone-pair electrons dominates.

No significant differences with the neutron parameters were observed for the positions of the C and N atoms as determined in the refinement of all X-ray data.

(b) Thermal parameters

In contrast to results of previous studies (Coppens, 1968*a, b*), temperature parameters obtained from the refinement of the neutron data are higher than X-ray thermal parameters. The relatively high values of the thermal parameters obtained earlier from room temperature X-ray studies (for which $\sin \theta/\lambda < 0.6 \text{ \AA}^{-1}$) have been ascribed to the tendency of the thermal parameters to compensate for the smearing out of valence electrons due to chemical bonding. The possibility for this compensation to occur decreases, however, when more high-order reflections are taken into account, as was done in the present work. For the present work, relatively good agreement was therefore expected between X-ray and neutron diffraction thermal parameters, especially for the X-ray refinements including high order reflections only. And indeed, Table 5 shows that good agreement is generally achieved between the thermal parameters of columns 5 (X-ray with $\sin \theta/\lambda > 0.6 \text{ \AA}^{-1}$), and 8 (neutron diffraction), apart from, however, a constant factor C between the two sets of values.

The constant factor between the X-ray and neutron thermal parameters is attributed to a difference between the two data-collection temperatures, and may be explained as follows.

Under the assumption of a harmonic-oscillator model for the translational motion of the molecules in the solid, the mean-square atomic displacement $\langle u^2 \rangle$ is given by

$$\langle u^2 \rangle = h[4\pi^2 m \nu]^{-1} [0.5 + \{\exp(h\nu/kT) - 1\}^{-1}]$$

where m is the mass of the vibrating body, ν is the frequency and h , k and T are respectively Planck's constant, Boltzmann's constant and the absolute temperature.

The displacements calculated with this expression are given as a function of temperature for a number of low-frequency modes in Fig. 3. The arrows in the Figure indicate the mean-square displacements corresponding to the principal elements of the rigid-body translation tensor as determined from the X-ray data. From the position of the arrows, it follows that the frequencies of the modes are between 40 and 60 cm^{-1} . In the temperature region of the experiments (about 100 °K), the mean-square displacements of the translational modes are linear with temperature within the approximation of the harmonic-oscillator model. A similar analysis for the librational modes shows that their frequencies are around 120 cm^{-1} ; therefore the mean-square displacements are again approximately proportional to the temperature. As the displacements of the high-frequency internal modes, which are temperature inde-

pendent in the liquid-nitrogen region, are small in comparison with those of the low-frequency modes, the ratio of the thermal parameters at temperatures T_1 and T_2 is given by $C = T_1/T_2$ in good approximation.

A good estimate of C was obtained by taking $C = \sum U_{ii}$ (X-ray); $\sin \theta/\lambda > 0.6 \sum U_{ii}$ (neutron). The value of 0.722 obtained in this way was slightly improved by considering the high-order X-ray coordinates ($\sin \theta/\lambda > 0.6 \text{ \AA}^{-1}$) and the neutron thermal parameters multiplied by C as fixed parameters in a scale factor refinement of the high order X-ray data. For $C = 0.728$ the value $K = 10.01$ obtained in the high-order refinement of all parameters was reproduced. A value of 0.728 for C implies that the temperature during neutron data collection was about 35° higher than during the parallel X-ray work.

About half of this temperature discrepancy can be explained by a difference between the temperatures at which the X-ray data were collected and the X-ray cell dimensions were measured (see section under choice of temperature).

The remainder of the difference in temperature factors could conceivably result from contraction of the atomic orbitals in the molecule. But, as mentioned earlier, no such evidence was found in previous room temperature studies, and it is considered more likely that the temperature of the neutron diffraction experiment was really 35° higher than during the collection of the X-ray data.

Several sets of X-ray parameters and the scaled neutron diffraction results are given in Table 5. Though it should be remembered that the scale of the neutron thermal parameters was obtained by comparison with the high-order X-ray data, the agreement between individual thermal parameters in the high-order and neutron sets is rather remarkable. The only significant discrepancy is shown by U_{22} of N(1).

The agreement is even more interesting in view of the many discrepancies found between the high-order ($\sin \theta/\lambda > 0.6 \text{ \AA}^{-1}$) and the low-order ($\sin \theta/\lambda < 0.6 \text{ \AA}^{-1}$) X-ray thermal parameters. In only two cases are the low-order diagonal elements U_{ii} lower than the corresponding high-order values, which confirms earlier experience with *s*-triazine and β -deutero-oxalic acid dihydrate (Coppens, 1968*b*). The two exceptions are the U_{11} values for the two carbon atoms. The refinement of electron population parameters, results of which are described elsewhere (Coppens, Csonka & Willoughby, 1970), suggests that these low U_{11} values are caused by the small population (compared to the spherically symmetric atom) of the p_π^2 orbital products on the carbon atoms.

The agreement between the *high-order* X-ray thermal parameters and the neutron diffraction results supports the validity of high-order refinement as a means to obtain thermal parameters free from bonding-effect errors. This procedure has been followed by Stewart & Jensen (1969) for uracil and by O'Connell (1969) for 2-aminoethylsulphonic acid; it should especially be

powerful when an appreciable amount of data can be collected beyond $\sin \theta/\lambda = 0.8 \text{ \AA}^{-1}$ (which was the limit for the cyanuric acid X-ray data).

(c) *Combined X-ray-neutron difference density*

As was done with earlier studies (Coppens, 1967; Coppens, Sabine, Delaplane & Ibers, 1969) the X-ray and neutron data were combined to obtain the function ρ_{X-N} , which represents the deviations from atomic spherical symmetry. A complication arises in the present study because of the 35° temperature difference between the neutron and X-ray experiment. It can be shown that the influence of this difference on the neutron coordinates is negligibly small, so that these parameters can be used with the X-ray data. The neutron thermal parameters, on the other hand, cannot be used for the calculation of the map. Instead, a 'best' set of thermal parameters was obtained by considering the neutron atomic coordinates as fixed parameters in a high order X-ray refinement based on the reflections with $\sin \theta/\lambda > 0.6 \text{ \AA}^{-1}$. The scale factor hardly changed during this refinement (from 10.01 to 10.03) and the temperature parameters agree to within two standard deviations with the high-order temperature parameters given in Table 5, the average discrepancy being less than one standard deviation.

The resulting map is shown in Fig. 4. Sharp, well defined maxima are observed in the C-N, C=O and C-H bonds and in the lone-pair region of the oxygen atoms. In comparison, with the regular X-ray difference map (Fig. 3 of Verschoor & Keulen, 1970) the maxima are higher. The differences are most pronounced for the

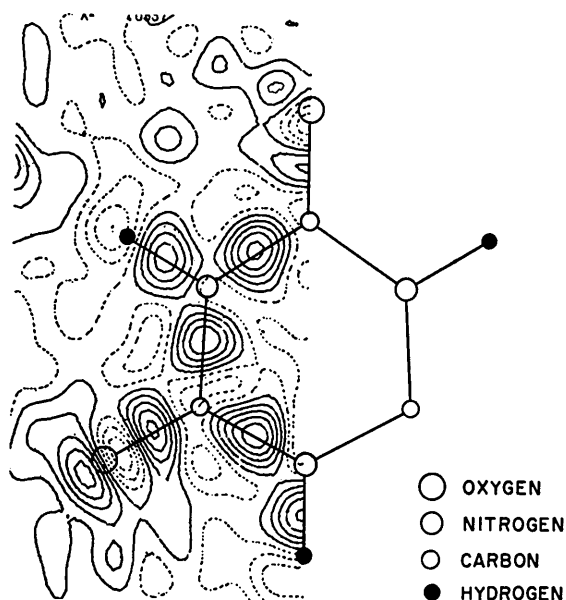


Fig. 4. Deviations from atomic spherical symmetry as given by the function ρ_{X-N} , the observed density minus the density calculated with spherical X-ray scattering factors, neutron positional parameters and a 'best' set of thermal parameters (see text). Section through the molecular plane; contours at $0.10 \text{ e.}\text{\AA}^{-3}$, negative contours dotted.

C=O and N-H bonds and for the oxygen lone-pairs, because of the significant differences between X-ray and neutron coordinates for the hydrogen and oxygen atoms.

The features are also stronger than those obtained earlier for triazine (Coppens, 1967) and deuterio-oxalic acid dihydrate (Coppens, Sabine, Delaplane & Ibers, 1969), where only local maxima were observed for the C-H and O-H bond, while in the present study we find the density in N-H to be of the same magnitude as the overlap charge in the C-O and C-N bonds. This improvement, if reproducible in other studies, may be typical for low-temperature studies.

The map illustrates the feasibility of charge density studies by diffraction methods, but what is clearly desired is a quantitative description of the features in terms of the population of atomic or molecular orbitals. Such an analysis is discussed in the next section.

(d) *Refinement of electron-density population parameters*

It has been proposed recently (Duckworth, Willis & Pawley, 1970) that the proper way to treat combined X-ray and neutron data is to use a single set of vibrational parameters and to allow for differences in coordinates by refining on both X-ray and neutron positional parameters simultaneously. A serious shortcoming of this treatment is that it does not account for the effect of atomic asphericity on the X-ray thermal parameters. The correct procedure is to use the neutron parameters, which are unaffected by bonding in the molecule, and to introduce explicitly the asphericity of the atomic charge density in the X-ray scattering factors (Stewart, 1969a; Coppens, 1969).

This method was recently developed further and has been applied to the diffraction data on α -deuterio-oxalic acid dihydrate and cyanuric acid. Preliminary results have been reported (Coppens, Csonka & Willoughby, 1970). A full account will be given in a subsequent publication.

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The Crystal Structures of Two Oxyfluorides of Molybdenum*

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Single crystals of the compounds $\text{MoO}_{2.4}\text{F}_{0.6}$ and $\text{Mo}_4\text{O}_{11.2}\text{F}_{0.8}$ were prepared by reacting MoO_3 and powdered Mo metal in the presence of HF under hydrothermal conditions at 500°C and 2 kbar pressure. $\text{Mo}_4\text{O}_{11.2}\text{F}_{0.8}$ is orthorhombic with space group *Cmcm*, $Z=4$, cell dimensions $a=3.878\pm 0.004$, $b=13.96\pm 0.01$, $c=3.732\pm 0.005$ Å. The measured and calculated densities are $d_m=4.6\pm 0.1$ and $d_c=4.70$ g.cm⁻³. The intensity data were collected by the Weissenberg method and the structure refined by least-squares to a final *R* value of 9.1% for 465 independent reflections. The structure is related to the MoO_3 structure with the Mo atom in a very distorted octahedral coordination. $\text{MoO}_{2.4}\text{F}_{0.6}$ is cubic with space group *Pm3m*, $Z=1$, cell dimension $a=3.842\pm 0.003$ Å, measured and calculated densities of $d_m=4.1\pm 0.1$ and $d_c=4.22$ g.cm⁻³. The intensities were measured by powder diffractometry and the *R* value based on intensities for 20 reflections was 12%. The structure is similar to the ReO_3 structure with the Mo atom in a normal octahedral coordination.

Introduction

Extensive studies on the structural chemistry of the molybdenum and tungsten oxide systems have been reviewed by Anderson & Magnéli (1950); Hägg & Magnéli (1954) and Kihlberg (1963). The structures of MoO_2 and MoO_3 , as well as those of a number of intermediate oxides, have been established. The basic building unit for these structures is a distorted MoO_6 octahedron; however, the degree of distortion may be large

enough to alter significantly the number of neighbors nearest to the molybdenum atoms.

It was first suggested by Magnéli (1956) that an increase in the amount of reduced molybdenum present in the compound is accompanied by an increase in the coordination number of the molybdenum atoms. In the MoO_3 structure the molybdenum atoms have a strong tendency toward fourfold coordination. However, in $\text{Mo}_{18}\text{O}_{52}$ the average number of oxygen atom near-neighbors approaches five, and in Mo_4O_{11} the coordination number of the molybdenum atoms approaches six.

In addition, Wilhelmi (1969) has recently determined the structure of $\text{Mo}_4\text{O}_{10}(\text{OH})_2$ and found it to be closely related to those of MoO_3 and $\text{Mo}_{18}\text{O}_{52}$. In the case of $\text{Mo}_4\text{O}_{10}(\text{OH})_2$ reduced molybdenum has been intro-

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