determinations of this excess can be made. Existence of the higher oxides Ni_3O_4, Ni_2O_3 and even NiO_2 has been proposed. However, X-ray diffraction patterns obtained from these higher oxides do not reveal a structure different from that of NiO. They do indicate that with increasing state of oxidation the materials become increasingly amorphous.

A possibly related problem is how does bivalent nickel in pure NiO co-ordinate oxygen octahedrally. It has two too many electrons to form six d^2sp^3 bonds. One is therefore led to investigate the possibility of resonating structures. A square co-ordinated complex of dsp^2 bonds with partial ionic character resonating among the three possible square configurations about nickel would account for the observed magnetic moment corresponding to approximately 0·8 unpaired electrons. Removal of a nickel atom from the crystal removes two electrons from the crystal. These presumably are supplied by one or two of the nickel ions nearest the vacant lattice site with the production of higher valent nickel and an approach to the formation of d^2sp^3 bonds. Equilibrium concentrations of interior lattice vacancies are not known but obviously in the extreme oxide (with composition near NiO_2) most of the vacant lattice sites must be on the crystal boundaries; that is to say, the crystal tends toward the amorphous state.

Much of the above work followed suggestions made by others at these laboratories. In particular the author wishes to acknowledge F. Morin (who also contributed measurements of magnetic susceptibilities), L. Wooten, K. Storks, Mrs E. A. Wood, and P. Anderson.

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The Structure of Millon's Base and its Salts

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The structure of Millon's base, $Hg_2NOH.2H_2O$, consists of a three-dimensional framework Hg_2N^+ in an idealized cristobalite type of arrangement. The mercury atoms form linear sp bonds, while the nitrogen forms tetrahedral sp^3 bonds, in a face-centered cubic lattice with $a = 9·58$ A. The Hg–N bond distance is $2·07_3$ A.

In the course of a study of reactions between mercury (I) compounds and ammonia (Arora, Lipscomb & Sneed, 1951), a sample of Millon's base, $Hg_2NOH.2H_2O$, was prepared. A powder diffraction pattern was taken, and has now been analyzed to yield the essentials of the structure of this compound.

Experimental results

The sample was placed inside a pyrex capillary about 0·2 mm. in diameter, and powder photographs were taken in a cylindrical camera of 5·73 cm. radius. Integrated intensities of the lines were estimated by a combination of micro-photometer tracings and visual estimates, and corrections were applied to these intensities, but not to the spacings, for the effect of absorption by the sample (*Internationale Tabellen*, 1935, vol. 2, p. 583).

Because initial attempts to index the pattern failed, a radial distribution function was prepared. The expression (Waser & Schomaker, 1945)

$$rD(r) = \sum_i \frac{I_i \sin 2\theta_i}{1 + \cos^2 2\theta_i} \exp\left[-3\frac{\sin^2 \theta_i}{\lambda^2} \right] \sin 2\pi h_i r,$$

where $h_i = 2 \sin \theta_i / \lambda$, was summed at intervals of 0·1 A. in r to give the result shown in Fig. 1. The function shows three clearly resolved peaks at 3·4, 5·9 and 6·9 A. These distances are nearly what would be expected from Hg...Hg distances in the configurations

and
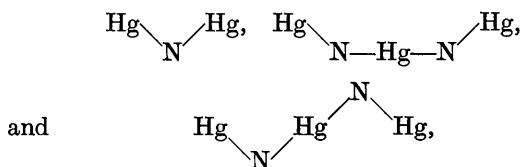
which, for an Hg–N bond distance of 2·07 A. and tetra-hedral configuration about the nitrogen atoms, would give 3·38, 5·86 and 6·77 A., respectively, for these peaks. Then, on the assumption that mercury forms linear sp bonds and that nitrogen forms tetrahedral sp^3 bonds, the various idealized SiO_2-types of arrangement were
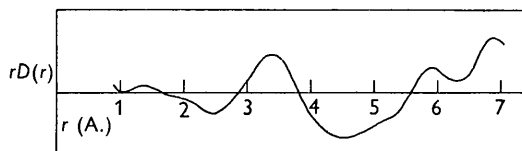

Fig. 1. Radial distribution function.

tested for agreement of spacings and intensities for the Hg_2N^+ part of the structure. Although the quartz and tridymite arrangements produced no agreement, the cristobalite type of structure was found to be in excellent agreement with both the intensities and spacings as shown in Table 1.

Table 1. *Diffraction data for* $Hg_2NOH.2H_2O$

hkl	$d_{obs.}$(A.)	$d_{calc.}$(A.)	$I_{obs.}$	$I_{calc.}$
111	5·518	5·530	237	131
311	2·884	2·888	65	71
222	2·757	2·765	131	87
400	2·395	2·394	48	45
331	2·198	2·197	43	35
511, 333	1·842	1·843	24	28
440	1·693	1·693	41	31
531	1·619	1·619	36	26
533	1·459	1·460	8	9
622	1·443	1·443	42	37
444	1·383	1·382	11	10
711, 511	1·341	1·341	15	13
731, 553	1·247	1·247	17	16
800	1·196	1·197	6	4
733	1·171	1·170	5	4
751, 555	1·106	1·106	8	8
662	1·100	1·098	16	13
840	1·072	1·071	14	12
911, 753	1·053	1·051	11	8
931	1·004	1·004	3	5
844	0·978	0·977	13	10
933, 771, 755	0·963	0·962	11	7
951, 773	0·926	0·926	5	7
10.2.2, 666	0·922	0·921	16	13
953	0·894	0·893	4	6
11.1.1, 775	0·865	0·864	4	6
880	0·848	0·846	4	6
11.3.1, 971, 955	0·838	0·837	16	17
11.3.3, 973	0·812	0·813	3	9
10.6.2	0·811	0·809	21	29
12.0.0, 884	0·799	0·798	14	20
11.5.1, 777	0·790	0·790	5	9

The mercury atoms are thus placed at $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}; \frac{1}{8}, \bar{\frac{1}{8}}, \bar{\frac{1}{8}};$ $\bar{\frac{1}{8}}, \frac{1}{8}, \bar{\frac{1}{8}}$ and $\bar{\frac{1}{8}}, \bar{\frac{1}{8}}, \frac{1}{8}$ plus the face-centered permutation, and the nitrogen atoms are placed in the diamond arrangement at 0, 0, 0 and $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ plus the face-centered permutation. The space group is T_d^2–$F\bar{4}3m$, and the lattice parameter is 9·58 ± 0·01 A., as determined from careful measurements on a film taken with use of the Straumanis technique. Calculation of the intensities

was made only from the positions of the mercury atoms with the use of the form factor (*Internationale Tabellen*, 1935, vol. 2, p. 573) multiplied by the temperature factor $\exp[-1\sin^2\theta/\lambda^2]$. The usual Lorentz-polarization factors and multiplicity factors were included. It may be remarked that all of those reflections due to the special positions of the mercury atoms are observed and no others. The cell thus contains eight $Hg_2NOH.2H_2O$ units, and gives a calculated density of 7·1 g.cm.$^{-3}$ in fair agreement with our observed value of 7·9 g.cm.$^{-3}$. Sidgwick (1950, vol. 1, p. 318) reports a value of 8·52 g.cm.$^{-3}$ for Hg_2NOH.

Because of the high background near the center of the films a large error was made in the estimation of the (111) reflection. This error is almost entirely responsible for the dip of the radial distribution curve below the zero line in the central region of Fig. 1.

Discussion

The scattering powers of all atoms except mercury are relatively so small that their positions can only be inferred. The Hg_2N^+ three-dimensional framework contains large channels in which it is presumed that the negative ions and water molecules are more or less randomly situated in such a way as to satisfy the electrostatic valency and the steric requirements.

With respect to the base and its salts we have found that photographs of $Hg_2NOH.2H_2O$ are substantially identical with those of $Hg_2NCl.H_2O$, Hg_2NCl, $Hg_2NBr.H_2O$, Hg_2NI, Hg_2NNO_3 and Hg_2NClO_4. Probably the amounts of water are not really definite, but merely enter the structure in inexact proportions (see Sidgwick, 1950, vol. 1, p. 318).

The Hg–N distance in $Hg_2NOH.2H_2O$ is 2·073 ± 0·003 A. Determinations of HgX bond lengths have been reported (Gregg, Hampson, Jenkins, Sutton & Sutton, 1937)* for the gaseous molecules $HgCl_2$ (2·34 A.), $HgBr_2$ (2·44 A.) and HgI_2 (2·61 A.). If one subtracts from these bond lengths the covalent radii of Cl (0·99 A.), Br (1·14 A.) and I (1·33 A.) (Pauling, 1940, p. 164), the sp radii 1·35, 1·30 and 1·28 A. for Hg are obtained. When the average of these values, 1·31 A., is added to the nitrogen covalent radius, 0·70 A., the predicted Hg–N distance of 2·01 A. is still somewhat less than the observed value of 2·073 A. No explanation of this effect is offered except possibly that the electronegativity difference in the bond may be less than average, or that the bonding of the negative ions in Millon's base and its salts may weaken the Hg–N bonds slightly.

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* A value of 2·27 ± 0·03 A. is reported (Maxwell & Moseley, 1940) for the Hg–Cl distance in gaseous $HgCl_2$.

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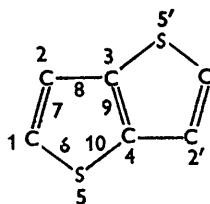WASER, J. & SCHOMAKER, V. (1945). *J. Amer. Chem. Soc.* 67, 2014.

Length of Central Bond in Thiophthen*

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Longuet-Higgins (1950) has suggested that the central bond, 9, in the thiophthen molecule

is compressed by bond angle stresses, and, by a consideration of the cumulative strains around $C_3=C_4$, has calculated that the amount of this compression is 0·06 A., in agreement with the 0·05 A. discrepancy between the observed bond length (Cox, Gillot & Jeffrey, 1949) and Evans & de Heer's (1949) semi-theoretical estimate. If the suggested effect were so large in thiophthen, it might be important also in many other cyclic molecules for which it has likewise hitherto been neglected (presumably because the force constants of bond-bending are ordinarily regarded as much smaller than those of bond-stretching), and, indeed, Longuet-Higgins's method of calculation, which in effect neglects the angle strains at 2, 5, 2' and 5', would indicate a bond compression whenever the adjacent interior bond angles are constrained below their normal values. However, consideration of such a simple case as the symmetrical four-membered ring of cyclobutane, for which the tensile stress due to the opposite-angle strains obviously balances the compressive stress due to the adjacent angle strains, shows this method of calculation to be quite wrong as well as incomplete, and implies that Longuet-Higgins's interesting suggestion cannot ac-

count for the distance anomaly in thiophthen and will not prove fruitful except for rings which are *suitably* unsymmetrical as well as highly strained.

Consider a planar n-ring with potential function $V(q_1, ..., q_{2n})$, in which the first n co-ordinates are the interior bond angles and the last n the bond lengths. The equations of static equilibrium may be written as

$$\frac{\partial V}{\partial q_i} + \lambda\xi_i + \mu\eta_i + \nu\zeta_i = 0,$$

and the auxiliary equations of ring closure, in first approximation, as

$$\Sigma\xi_i(q_i - q_i^0) = 0 \quad (x \text{ component}),$$
$$\Sigma\eta_i(q_i - q_i^0) = 0 \quad (y \text{ component}),$$
and
$$\Sigma\zeta_i(q_i - q_i^0) = 0 \quad (\text{angle sum}),$$

the three redundancies being handled by means of the Lagrangean multipliers λ, μ, and ν. If the positive direction of a bond is counter-clockwise and the Cartesian co-ordinates of the atom at a bond angle q_i are $x_i, y_i (i = 1, ..., n)$ relative to an arbitrary origin, the quantities ξ_i, η_i and ζ_i may be written as $\xi_i = -y_i$, $\eta_i = x_i$, and $\zeta_i = 1$ for $i = 1, ..., n$ and $\xi_i = \cos(\overrightarrow{r_i}, \overrightarrow{OX})$, $\eta_i = \sin(\overrightarrow{r_i}, \overrightarrow{OX})$, and $\zeta_i = 0$ for $i = n+1, ..., 2n$.

If the Cartesian co-ordinate axes are rotated by the angle

$$\theta_0 = \cos^{-1}[\lambda/\sqrt{(\mu^2 + \nu^2)}] = \sin^{-1}[\mu/\sqrt{(\lambda^2 + \mu^2)}]$$

to give transformed Cartesian atomic co-ordinates x_i', y_i', the equations of equilibrium reduce to

$$\frac{\partial V}{\partial q_i} - \sqrt{(\lambda^2 + \mu^2)}\, y_i' + \nu = 0, \quad i = 1, ..., n,$$

and

$$\frac{\partial V}{\partial q_i} + \sqrt{(\lambda^2 + \mu^2)} \cos(\overrightarrow{r_i}, \overrightarrow{OX'}) = 0, \quad i = n+1, ..., 2n,$$