infrared spectrum corresponding to the Raman band at 1040 cm^{-1}, characteristic of uncomplexed nitrate, the infrared spectrum of a dilute solution of mercury(II) nitrate has a band at 1032 cm^{-1} instead of the bands at 1023 and 986 cm^{-1} observed for the saturated solutions.

The assignments of the infrared and Raman bands observed for the mercury(II) nitrate monohydrate plus potassium nitrate mixture are summarized in Table II.

Acknowledgments.—This work was supported by grants from the National Research Council of Canada and by the Government of Ontario in the form of an Ontario Graduate Fellowship to A. R. D. The technical assistance of Mrs. J. Weerheim in some aspects of the work and the assistance of the staff of the Computer Science Division of the University of Waterloo are also gratefully acknowledged.

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New Ternary Oxides of Mercury with the Pyrochlore Structure

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Three new ternary oxides of mercury—$Hg_2Nb_2O_7$, $Hg_2Ta_2O_7$, and $Hg_2Sb_2O_7$—have been prepared and characterized. All three have the cubic pyrochlore structure with cell edges of 10.453, 10.452, and 10.349 Å, respectively. The structure of $Hg_2Nb_2O_7$ was refined by least-squares to an R of 0.027 using 26 reflections collected with a powder diffractometer. It is shown that the pyrochlore structure may be visualized as two interpenetrating networks, one network being identical with one of the two interpenetrating networks in Cu_2O.

Introduction

Very little is known about ternary oxides of mercury. A recent excellent review on mercury compounds by Aurivillius[1] discusses several oxyhalides of mercury; however, the only ternary oxides mentioned are of the type A_2HgO_2 where A is an alkali metal. One reason for the apparent lack of knowledge about ternary oxides of mercury is that the preparation by usual solid-state methods is hampered by the ease with which mercury is reduced to the metal.

In various mercury oxide compounds mercury has frequently been found[1] in essentially linear, twofold coordination. This paper describes the preparation and characterization of three new ternary oxides of mercury where mercury is again in essentially linear, twofold coordination.

Experimental Section

Reactants.—Niobium and tantalum pentoxide were prepared by oxidizing, at 600° in air, Specpure metals obtained from Johnson, Matthey & Co. Antimony sesquioxide was reagent grade, and Specpure mercuric oxide was obtained from Johnson, Matthey & Co.

Syntheses.—The reactants were intimately mixed in appropriate amounts by grinding together in an agate mortar and pestle. The preparation of $Hg_2Sb_2O_7$ was conveniently carried out by heating the reactants at 500° for 2 days in an open silica boat under about 1 atm of oxygen. When this method was attempted for $Hg_2Nb_2O_7$ and $Hg_2Ta_2O_7$, all of the mercuric oxide separated from the other oxide; consequently, a closed system was used. For $Hg_2Nb_2O_7$ and $Hg_2Ta_2O_7$, appropriate amounts of the mixed reactants were pelleted, sealed in evacuated silica tubes, and heated at 500° for 2 days.

In high-pressure experiments, the preformed compounds or reactant mixtures were sealed in pressure-collapsible gold containers. $Hg_2Nb_2O_7$ and $Hg_2Ta_2O_7$ were most conveniently prepared at 700° and 3 kbars. The apparatus used in the 60-kbar experiments has been previously described by Bither, *et al.*[2]

Analyses were carried out by standard techniques, and densities (d, g/cm^3) were determined using a pycnometer. *Anal.* Calcd for $Hg_2Nb_2O_7$: Hg, 57.4; Nb, 26.6; O, 16.0; d, 8.128. Found: Hg, 56.8; Nb, 26.8; O, 15.8; d, 8.10. Calcd for $Hg_2Ta_2O_7$: Hg, 45.8; Ta, 41.4; O, 12.8; d, 10.179. Found: Hg, 45.1; Ta, 42.1; O, 13.1; d, 10.13. Calcd for $Hg_2Sb_2O_7$: Hg, 53.0; Sb, 32.2; O, 14.8; d, 9.067. Found: Hg, 52.9; Sb, 32.0; O, 14.5; d, 9.02. Errors for the densities are considered to be about ±0.06 g/cm^3.

X-Ray Analyses.—Integrated X-ray powder data were gathered with a General Electric XRD-5 diffractometer using Cu Kα radiation, an Ni filter, a scintillation detector, and a pulse height analyzer. The intensity of each peak was determined by scanning at 0.2°/min and accumulating both time and counts. Background was determined before the first peak, between every two peaks, and after the last peak. The values obtained were plotted against 2θ, and a smooth curve was drawn through the points. The background function of 2θ was not monotonic; *e.g.*, there were minima at ~23 and 40° (2θ). The background corrections obtained from this curve are similar to but more reliable than those which would be obtained by assuming a strictly linear interpolation between backgrounds determined on the two sides of the peak.

The sample was prepared by grinding in a mechanical mortar and pestle for several hours and then passing it through a 400-mesh sieve. The powder was packed in a tray by several different methods and X-ray data were taken to determine if preferred orientation was a serious problem. Comparison of the several sets of data led to the conclusion that preferred orientation was not significant. This conclusion was further supported by the visual observation of no qualitative differences between the diffractometer and Debye-Scherrer patterns. The depth of the flat sample tray was about 1 mm, which effectively prohibits any X-rays from passing through the sample. The di-

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(1) K. Aurivillius, *Arkiv. Kemi*, **24**, 151 (1965).

(2) T. A. Bither, J. L. Gillson, and H. S. Young, *Inorg. Chem.*, **5**, 1559 (1966).

mensions of the tray and beam slits were such that the entire beam was intercepted by the sample for all peaks.

The intensity of a group of equivalent reflections was taken to be $I = F^2S(\mathrm{Lp})M$, where F is the structure factor, S is the scale factor, Lp is the usual Lorentz-polarization factor, and M is the multiplicity factor. The observed intensity is compared to the sum of calculated intensities which fall at the same, or nearly the same, value of 2θ. The scattering factors for Hg^{2+} and Nb^{5+} were taken from Cromer and Waber.[3] Tokonami's[4] scattering factor for O^{2-} was used. Real and imaginary anomalous dispersion corrections were made, and these were taken from Cromer.[5]

Cell dimensions for $Hg_2Nb_2O_7$, $Hg_2Ta_2O_7$, and $Hg_2Sb_2O_7$ were determined from Debye–Scherrer films taken at 25°. A least-squares refinement used the Nelson–Riley function and assumed $\lambda(\mathrm{Cu}\ K\alpha_1)$ 1.54051 and $\lambda(\mathrm{Cu}\ K\alpha_2)$ 1.54434 Å.

Crystallography of the Pyrochlore Structure

The space group for the ideal pyrochlore structure is Fd3m. There are four crystallographically non-equivalent kinds of atoms, and the general pyrochlore formula may be written as $A_2B_2O_6O'$, where $Z = 8$. There are four possible choices of origin; two are referred to the centric origin of Fd3m, and two refer to $\bar{4}3m$ as the origin. All four origins have been used, and this has led to some unfortunate consequences. Either the A or B cation may be placed at the origin, and these choices will be referred to as A_o and B_o, respectively. A third choice, O_o, is to place O′ at the origin; the fourth choice, V_o, is to have no atom at the origin. The choices A_o and B_o are generally to be preferred since for these choices there is a center of symmetry at the origin. Thus, the A atoms are in 16c and the B atoms in 16d with the O′ atoms in 8a, or, alternately, the B atoms are in 16c and the A atoms in 16d with the O′ atoms in 8b. In any case the remaining oxygen atoms are in 48f.

The systematic absences for the pyrochlore structure are more specific than the general absences for space group Fd3m. The additional rules are that for *hkl* reflections h, k, and l must equal $4n + 2$ or $4n$, or $h + k + l$ must equal $2n + 1$ or $4n$.

The first choice of origin used[6] was apparently V_o. Later, according to Wyckoff,[6] "a significantly different arrangement" was suggested for the pyrochlore (or atopite) type. Actually the first structure [proposed for $(Ca,Mn,Na)Sb_2(O,OH,F)_2$] was undoubtedly wrong since for V_o the A atoms should be in 16d instead of 16c. The oxygen positional parameter is within the range expected for the V_o origin. Consequently, placing A atoms in 16c results in the implausible situation where the larger A atoms have the smaller coordination and the shorter metal-to-anion bonds. The origin at O_o was used for $Ca_{1.56}Sb_2O_{6.37}F_{0.44}$[7] and $Tl_2Pt_2O_7$.[8] For $Cd_2Nb_2O_7$[9] and $Cd_2Re_2O_7$[10] the origin was taken at B_o, and for $Er_2Ti_2O_7$[11] the origin was taken at A_o.

The pyrochlore structure has only one positional parameter, and there are simple rules to convert the value of this parameter depending on the choice of origin. For example, on the basis of the first position of 48f given in the "International Tables for Crystallography," $x(A_o) = {}^3/_4 - x(B_o)$, $x(V_o) = {}^1/_2 - x(O_o)$, $x(O_o) = x(A_o) - {}^1/_8$, and $x(V_o) = {}^5/_8 - x(A_o)$. In any case x may be replaced with ${}^1/_4 - x$.

Results

Refinement of $Hg_2Nb_2O_7$.—No single crystals were obtained for $Hg_2Ta_2O_7$, $Hg_2Nb_2O_7$, or $Hg_2Sb_2O_7$. However, since there is only one positional parameter for the pyrochlore structure, 26 intensities collected from the powder for $Hg_2Nb_2O_7$ were considered adequate. Reflections for which the total net count of a peak was less than background plus the square root of the background were considered unobservable. The least-squares refinement of the data used a full-matrix program,[12] SFLS6, adapted for powders. σ values were taken to be $\sqrt{I_o} + 10$, and the function $w(I_o - I_c)^2$ was minimized.

Several cycles of refinement of the scale factor, positional parameter, and individual isotropic temperature factors led to an R of 0.031 and a wR of 0.043. The temperature factor of O′ became slightly negative and was therefore fixed at 0.2. Further refinement of anisotropic temperature factors for Hg led to a final R of 0.027 and a wR of 0.034. The site occupancies of the Hg site and the O′ site were refined and both were found to be 1.0 within their standard deviations. The origin had been taken at B_o with O′ thus in position 8b. The only other site which could reasonably be occupied to any extent was position 8a. A trial oxygen was placed in this position, and its site occupancy was quickly refined to 0.0 within its standard deviation.

Since anisotropic temperature factors have apparently not previously been refined with powder data, some justification for their use may be necessary. For positions 16c and 16d (the A and B atoms), $\beta_{11} = \beta_{22} = \beta_{33}$ and $\beta_{12} = \beta_{13} = \beta_{23}$. Thus, changing from isotropic to anisotropic temperature factors leads to only one more parameter for each of these atoms. The B atom is in nearly octahedral coordination and therefore would be expected to be essentially isotropic. For niobium the refined cross terms (β_{12}, β_{13}, and β_{23}) were found to be 0.0 within their standard deviations; consequently, the B atom was fixed as isotropic. For the A atom (Hg), which is the heaviest atom in the structure and had the largest isotropic thermal parameter, the cross terms refined to values which were well outside their standard deviations (Table I). The hypothesis that mercury is really vibrating isotropically within the accuracy of these data was tested

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(3) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

(4) M. Tokonami, *ibid.*, **18**, 486 (1965).

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

(6) R. W. G. Wyckoff, "Crystal Structures," 2nd ed, Interscience Publishers Inc., New York, N. Y., 1965, p 439.

(7) M. A. Aia, R. W. Mooney, and C. W. W. Hoffman, *J. Electrochem. Soc.*, **110**, 1048 (1963).

(8) H. R. Hoekstra and S. Siegel, *Inorg. Chem.*, **7**, 141 (1968).

(9) F. Jona, G. Shirane, and R. Pepinsky, *Phys. Rev.*, **98**, 903 (1955).

(10) P. C. Donohue, J. M. Longo, R. D. Rosenstein, and L. Katz, *Inorg. Chem.*, **4**, 1152 (1965).

(11) O. Knop, F. Brisse, L. Castelliz, and Sutarno, *Can. J. Chem.*, **43**, 2812 (1965).

(12) C. T. Prewitt, unpublished computer program.

TABLE I

FINAL POSITIONAL AND THERMAL PARAMETERS[a] FOR $Hg_2Nb_2O_7$

Atom	x	y	z	B^b
Hg	0.5	0.5	0.5	1.4 ± 1
Nb	0.0	0.0	0.0	0.5 ± 1
O	0.323 ± 2	0.125	0.125	0.9 ± 8
O′	0.375	0.375	0.375	0.2

[a] Positional parameters are expressed as fractions of the cell edge and the errors given apply to the last significant place. [b] The final anisotropic thermal parameters for Hg are $\beta_{11} = \beta_{22} = \beta_{33} = 0.0033 \pm 2$ and $\beta_{12} = \beta_{13} = \beta_{23} = -0.0016 \pm 4$. The isotropic thermal parameter given for Hg is actually the isotropic equivalent.

TABLE II

OBSERVED AND CALCULATED INTENSITIES FOR $Hg_2Nb_2O_7$[a]

h k l	I_{obs}	I_{calc}	h k l	I_{obs}	I_{calc}	h k l	I_{obs}	I_{calc}
1 1 1	811	790	8 0 0	498	531	9 5 3	-	24
2 2 0	-	44	7 3 3	73	48	10 4 2	-	6
3 1 1	813	830	6 6 0		<1	11 1 1		
2 2 2	10492	10349	8 2 2		16	7 7 5		
4 0 0	3590	3675		-	16		-	33
3 3 1	900	842	5 5 5		9	8 8 0	306	350
4 2 2	-	40	7 5 1		102	9 5 5		2
3 3 3		2	6 6 2		1382	9 7 1		55
5 1 1		400		1440	1492	11 3 1		17
	373	402	8 4 0	1146	1194		75	74
4 4 0	4150	4205	7 5 3		87	10 6 0		31
5 3 1	341	301	9 1 1		11	8 6 6		5
6 2 0	-	19		119	98		-	36
5 3 3		88	6 6 4	-	16	9 7 3		34
6 2 2		3957	9 3 1	31	41	11 3 3		<1
	4031	4045	8 4 4	875	926	10 6 2		1466
4 4 4	1023	1021	7 5 5				1620	1500
5 5 1		6	9 3 3			12 0 0		163
7 1 1		88	7 7 1			8 4 4		823
	116	94		92	81		1004	986
6 4 2	-	3	10 2 0		<1	11 5 1		28
7 3 1		37	8 6 2		<1	7 7 7		<1
5 5 3		76		-	<1		-	28
	109	114	7 7 3		1	12 2 2	-	3
			9 5 1		17	10 6 2	-	6
			10 2 2		797	9 7 5		56
			6 6 6		271	11 5 3		44
				1099	1086		71	100

[a] Observed intensities are grouped in the case of unresolved nonequivalent reflections. The sum of these peaks is given immediately following such a group and is compared with the sum of the calculated intensities.

using Hamilton's[13] $\mathcal{R}$ ratio. The dimension of this hypothesis is 1, and $\mathcal{R}_{1,20,0.005} = 1.224$. The experimental value of $\mathcal{R}$ is $0.043/0.034 = 1.26$. Thus according to this test, there is less than a 0.5% probability that the mercury anisotropic temperature factors are without significance.

The A atom is on the cube threefold axis, and its thermal ellipsoid is an ellipsoid of rotation where the unique axis is the threefold axis. The ellipsoid thus must be elongated or shortened along this axis. The thermal ellipsoid with errors was calculated[14] and was found to be shortened along the threefold axis. The rms displacement along the axis is 0.02 ± 0.04 Å, and for an arbitrary vector perpendicular to this axis the rms displacement is 0.165 ± 0.005 Å. Since there are two very short bonds along the threefold axis, this result, which indicates predominant thermal motion perpendicular to these bonds, is physically reasonable.

The final positional and thermal parameters are given in Table I, and the observed and calculated intensities are in Table II. The scale factor, S, is 0.393×10^{-4}. Selected interatomic distances and angles were calculated[14] and are given in Table III. The O–Nb–O angles are a measure of the distortion of the niobium–oxygen octahedra since these angles would, of course, all be 90° if the octahedra were regular.

Chemical and Physical Properties.—For each of the compounds—$Hg_2Nb_2O_7$, $Hg_2Ta_2O_7$, and $Hg_2Sb_2O_7$—variations in both cell dimensions and color were noted. The variation in cell dimensions, over about 0.02 Å, was definitely outside experimental error and probably resulted from slight nonstoichiometry. The nonstoichiometry was not investigated in detail; however, in samples apparently slightly deficient in mercury and oxygen, the pyrochlore phase was red to black and the cell size was decreased. The most nearly stoichiometric phases of $Hg_2Nb_2O_7$ and $Hg_2Ta_2O_7$ were yellow while those of $Hg_2Sb_2O_7$ were brown. All data given in this paper refer to the most stoichiometric phases obtained.

Thermogravimetric measurements indicated that decompositions under atmospheric conditions began at about 500° for HgO, $Hg_2Nb_2O_7$, and $Hg_2Ta_2O_7$ but did not begin until about 700° for $Hg_2Sb_2O_7$. Samples of the three mercury pyrochlores which were quenched from 900° and 60 kbars still showed the pyrochlore structure.

TABLE III

SELECTED INTERATOMIC DISTANCES AND ANGLES FOR $Hg_2Nb_2O_7$

Distance	Å	Angle	Deg
Hg–O	2.61 ± 1		
Hg–O′	2.2631 ± 3	O′–Hg–O′	180.0
Nb–O	1.999 ± 8	O–Nb–O	94.1 ± 8
O–O	4.00 ± 2	O–Nb–O	85.9 ± 8
O–O	2.72 ± 1	Hg–O′–Hg	109.5
O–O′	3.16 ± 2		
O–O′	3.735 ± 3		

Since $Cd_2Nb_2O_7$ is known to be ferroelectric,[9] the electrical properties of $Hg_2Nb_2O_7$ and $Hg_2Ta_2O_7$ were studied despite their apparent cubic and centrosymmetric space group. However, the electrical resistivities of pellets of both samples were only about 10^3 ohm-cm at room temperature, and this was considered too low for a worthwhile investigation of dielectric properties. The activation energies of the two samples, determined from a log ρ *vs.* $1/T$ plot (100–208°K), were found to both be about 0.1 eV. These electrical properties might well be expected to vary strongly with stoichiometry; however, this was not studied.

Discussion

Although the A cation in the pyrochlore structure is in eightfold coordination, there are six anions at one distance and two others at a closer distance. Some representative A-to-anion distances are given in Table IV. In Figure 1 the pyrochlore structure is shown with

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(13) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

(14) W. R. Busing, K. O. Martin, and H. A. Levy, ORNL-TN-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

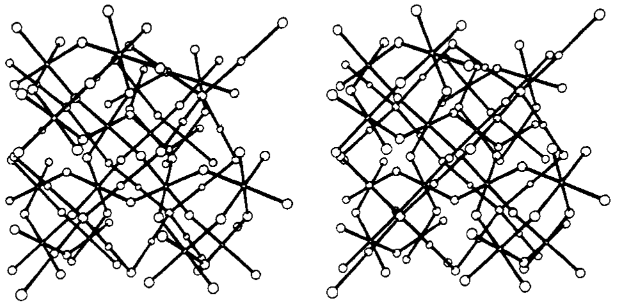


Figure 1.—The pyrochlore structure as two interpenetrating networks. The smallest atoms (B cations) are in octahedral coordination, the next largest atoms (A cations) are in linear coordination, and the remaining larger atoms are the anions. One unit cell is shown, and the view is nearly along the *a* axis.

TABLE IV

STRUCTURAL DATA FOR SOME PYROCHLORE PHASES

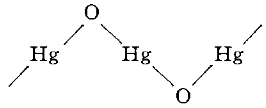
			Å			
Compound	Cell edge, Å	x^a	A–O′	A–O^b	B–O	Ref
$Cd_2Nb_2O_7$	10.372	0.305	2.25	2.67	1.92	9
$Cd_2Re_2O_7$	10.219	0.309	2.21	2.66	1.90	10
$Cd_2Ta_2O_7$	10.375	0.317	2.25	2.64	1.96	17
$Hg_2Sb_2O_7$	10.349	0.321	2.24	2.54	1.97	*d*
$Hg_2Nb_2O_7$	10.453	0.322	2.26	2.56	2.00	*c*
$Hg_2Ta_2O_7$	10.452	0.322	2.26	2.56	2.00	*d*
$La_2Zr_2O_7$	10.808	0.322	2.34	2.64	2.10	17
$Er_2Ti_2O_7$	10.076	0.330	2.18	2.47	1.96	11, 17
$La_2Hf_2O_7$	10.780	0.330	2.33	2.64	2.10	17
$Sm_2Sn_2O_7$	10.510	0.333	2.28	2.55	2.05	17
$Ca_{1.56}Sb_2O_{6.37}F_{0.44}$	10.300	0.338	2.23	2.47	2.04	7
$Tl_2Pt_2O_7$	10.132	0.355	2.19	2.32	2.08	8

[a] The oxygen positional parameter with the origin taken at the B cation (B_o). This value would be 0.3125 for a regular octahedron around B and would be 0.375 for a regular cube around the A cation. [b] There are two A–O′ and six A–O distances for each A cation. [c] This work. [d] The positional parameter (*x*) was determined from the assumed B–O distances.

only the shorter two A-to-anion distances drawn in as bonds. As may be seen, this results in two interpenetrating networks with one network identical with one of the networks in Cu_2O. The Cu_2O structure has frequently been described as two interpenetrating networks with no primary bonds between the two networks.[15,16]

In the A_2O network of the pyrochlore structure (or the Cu_2O structure), the cation is in linear coordination. The A-to-anion distances, unaffected by any positional parameter, can be established with knowledge of only the cell edge. In the BO_3 network, B is in octahedral coordination while the anion is in twofold coordination. A positional parameter determines the B-to-anion distances which must all be equal. The closest contact between the two networks is between the A cations of the A_2O network and the oxygen ions of the BO_3 network. However, these *internetwork* distances are always significantly longer than any *intranetwork* distances (Table IV). The anisotropic thermal behavior of Hg in $Hg_2Nb_2O_7$ further supports this two-network view in that essentially all of the thermal motion of the mercury is in the direction of the oxygens of the BO_3 network. This, of course, indicates that these six Hg–O bonds are indeed very weak compared to the bonds within the Hg_2O network.

Both HgO forms contain infinite zigzag chains[1] of the type



Mercury pyrochlores have the same chains, but they intersect at oxygen; thus, the coordination of oxygen is four instead of two. The Hg–O–Hg angle in HgO (both forms) is very close to 109° and in pyrochlores is, of course, exactly the tetrahedral value. The mercury coordination is two, and nearly linear, in HgO (both forms) and is two, and exactly linear, in the Hg_2O network of the pyrochlores. The Hg–O distances are somewhat longer in the pyrochlores than in HgO, *i.e.*, 2.25 *vs.* 2.03 Å; however, this presumably reflects the difference in oxygen coordination as well as the requirements of the BO_3 network.

The proposed two-network view of the pyrochlore structure becomes more appropriate as the cube around the A cation becomes increasingly distorted. When the origin is placed at the B cation (B_o), an x value of 0.375 would give a perfect cube around A. Thus, deviations from this value are a measure of the appropriateness of the two-network model. It is seen (Table IV) that this model is most appropriate when A is Cd or Hg but still has some validity for all of the other pyrochlores. It is interesting that $Ca_2Nb_2O_7$, $Ca_2Ta_2O_7$, and $Ca_2Sb_2O_7$ do not exist as pyrochlores[7,17] despite the fact that the ionic radius of Ca is intermediate between Cd and Hg. This may indicate that Ca is reluctant to adopt such a highly distorted cubic coordination which would be required for the ideal pyrochlore structure with realistic B–O distances.

A network view of the pyrochlore structure, as opposed to a fluorite derivative view, has been suggested by others.[9,17] However, the usual network approach to the pyrochlore structure stresses the BO_3 network and views the remainder as essentially interstitial. This one-network-plus-interstitials approach certainly is more valid than the two-network approach for some compounds. For example, some pyrochlore-type compounds have vacancies at A sites and also at special position oxygen sites.[9] Undoubtedly the most essential feature of the pyrochlore structure is the BO_3 network. However, the space remaining may be utilized in different ways. One very important way is a second interpenetrating network.

The oxygen positional parameter in the pyrochlore structure is found to range from 0.305 to 0.355 (Table IV) based on the origin at the B cation. A significantly different and incorrect range was recently given by

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(15) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 253–254.

(16) A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University, Press, London, 1962, pp 122–123, 460.

(17) F. Brisse, Ph.D. Thesis, Dalhousie University, Halifax, N. S., Canada, 1967.

Hoekstra and Siegel.[18] The upper limit of this range, 0.355, should be viewed with caution since it is based on one value which was not well determined. In any event, on the basis of currently available structural data, one limit for x in the pyrochlore structure is about midway between the values for an ideal cube around A and a regular octahedron around B. The other limit is just the other side of a regular octahedron around B.

Acknowledgment.—The author is indebted to C. T. Prewitt and P. C. Donohue for helpful discussions. The 60-kbar experiments were supervised by C. L. Hoover; the stereoscopic drawing of the pyrochlore structure was made by P. M. G. Wong using ORTEP, and the electrical measurements were made by P. E. Bierstedt.

(18) Hoekstra and Siegel (ref 8, Fig. 3) gave the limits of the oxygen positional parameter in the pyrochlore structure to be about 0.27–0.30, and these limits are presumably based on the authors' choice of origin, O_0. These limits correspond to a range of 0.355–0.325 on the basis of the origin at the B cation (B_0). It would appear that this incorrect range resulted from the indiscriminate use of x parameters from various pyrochlores where different origins were used and from the failure to transform such data to a common origin. Furthermore, the authors' conclusion that the pyrochlore structure has not been observed in the region of regular octahedra around the B cations is also incorrect.

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Raman Spectra and Structures of Arsenious Acid and Arsenites in Aqueous Solution[1]

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The molecular species of As(III) in aqueous solution have been studied by the Raman effect. Utilizing the Job method of continuous variation, solutions with $[OH^-]/[As(III)]$ between 3.5 and 15 have been shown to contain the four species $As(OH)_3$, $AsO(OH)_2^-$, $AsO_2(OH)^{2-}$, and AsO_3^{3-}. The Raman spectra are consistent with a C_{3v} point group assignment for both $As(OH)_3$ and AsO_3^{3-}. C_s symmetry has been shown for $AsO(OH)_2^-$ and probably for $AsO_2(OH)^{2-}$, although experimental data on the latter species were most difficult to obtain, since the spectra of all species are overlapped to a large extent. The As–O stretching vibrations, insensitive to D_2O, are between 790 and 750 cm^{-1}, whereas the symmetric As–OH stretching modes, all exhibiting an isotope effect, are at 710 cm^{-1} for $As(OH)_3$ and 570 cm^{-1} for $AsO(OH)_2^-$. The species $As(OH)_3$ is also identified from its Raman spectrum as the only major component in acidic aqueous solutions of $As_4O_6(s)$. The existence of $HAsO_2$ is ruled out. Furthermore, there is no evidence for polymerization in basic solutions within an [As(III)] range of 0.6–5.0 *M*.

Introduction

Little is known of the structure of arsenious acid or its ionized forms in aqueous solutions. For the weak acid a single dissociation constant has generally been reported ($pK_a \simeq 10$); this fact has given rise to the formulation $HAsO_2$, although no unambiguous structural evidence exists for this. In a recent summary of various properties of aqueous solutions of As(III), Jander and Hofmann[2] supported the existence of an equilibrium between $HAsO_2$ and H_3AsO_3 in solution. Their findings rule out the existence of any polymeric aqueous solution species for [As(III)] up to approximately 0.3 *M*. The structural aspects of arsenious acid are intriguing with respect to its congeners, nitrous and phosphorous acids. Nitrous acid, although not known in the liquid state, has a bent structure HO–N–O, whereas phosphorous acid corresponds to the formula $H_2(HPO_3)$ with a four-coordinate P atom. The existence of the H–P bond has been firmly established by the Raman spectrum of a phosphorous acid solution in which the H–P vibration is observed as well as by the proton resonance spectrum in which the P-bound hydrogen shows a considerable chemical shift away from bulk solvent protons.

The adaptability of the Raman technique to the study of arsenious acids was recognized by Fehér and Morgenstern.[3] These authors found no Raman line attributable to an As–H vibration but their photographically recorded spectra were insensitive to any spectral changes taking place upon addition of base to the weak acid. Furthermore, since the Raman spectrum of the ortho form (K_3AsO_3 in solution) was essentially the same as that of aqueous solutions of As_4O_6 + 4, 8, and 12 NaOH, they concluded that an equilibrium existed between the ortho and meta forms in which the latter predominates.

The pH and conductometric titrations of Bhatnagar and Govind,[4] however, again lend support to the existence of several arsenites in solution formed when the ratios of As_4O_6 to NaOH are 1:4, 1:8, and 1:12, respectively. The highest concentration studied, however, was 0.2 *M*. Thus, it appears still uncertain what stoichiometric species and what structural species actually exist in solutions of arsenites. The data of Bhatnagar and Govind support the pyro form (*i.e.*,

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(2) G. Jander and H. Hofmann, *Z. Anorg. Allgem. Chem.*, **296**, 134 (1958).

(3) F. Fehér and G. Morgenstern, *ibid.*, **232**, 177 (1937).

(4) C. S. Bhatnagar and K. Govind, *Z. Naturforsch.*, **21b**, 190 (1966).