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A Molecular Orbital Study of the Bonding in Bi_9^{5+} [1]

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The bonding in the homopolyatomic ion Bi_9^{5+} is considered in terms of the D_{3h} symmetry orbitals for 6p AO's and standard LCAO–MO calculations including overlap. The stability and diamagnetism of the cation is supported by the closed-shell MO configuration that results with the 22 p electrons in 11 bonding MO's. The bonding is further detailed in terms of the approximate charge distribution and bond orders. The possible existence of related isoelectronic ions with neighboring elements and the MO bonding scheme for the proposed D_{3h} ion Bi_3^{3+} are also considered.

Introduction

Certainly the most remarkable feature revealed by the recent determination[3] of the crystal structure of the so-called bismuth monochloride[4] is the presence of the unique homopolyatomic ion Bi_9^{5+}. This cation is found in the compound with two types of chlorobismuthate(III) anions in the proportions $(Bi_9^{5+})_2(BiCl_5^{2-})_4(Bi_2Cl_8^{2-})$ so that the stoichiometry is actually $BiCl_{1.167}$. Obviously the character of the bonding in this diamagnetic species is of considerable importance in understanding its existence as well as in providing information as to where related structures may be encountered. Since considerable delocalization of the bonding electrons is indicated by both the fractional oxidation state of the bismuth and the relatively high symmetry of the group, the two-center basis of a valence bond description does not seem particularly useful. On the other hand, the simplicity of LCAO–MO methods makes them especially applicable to such problems,[5] and this kind of treatment follows.

Symmetry Properties

The Structure.—The atomic arrangement in Bi_9^{5+}, Fig. 1, may be described as a trigonal prism 1–2–3, 4–5–6 plus the three atoms 7–8–9 outside the rectangular faces of the prism on its C_2 axes, or, alternatively, as three rectangular pyramids with apices at atoms 7, 8, and 9 that share opposite, basal edges. In order to gain as much as possible from symmetry the ion is assumed to have full D_{3h} symmetry. This is by no means a drastic assumption. Although the cation as found in the crystal is somewhat distorted and nearer C_{2v} symmetry, as discussed earlier,[3] this appears to be a simple consequence of the low symmetry of the approximately close-packed anions. The result is that substantially only one edge of the prism (*e.g.*, 1–4) is elongated by about 7.5%; distances to the neighboring face atoms (7 and 8) are scarcely affected by this distortion and, instead, the adjustment is largely in the angles at these points. Assuming this interpretation of the real structure is correct, the distances in the ideal cation needed later were taken from those observed in the remainder of the cation and are: 1–2, 3.18 Å., 1–7, 3.09 Å., and 1–4, 3.70 Å.

A second necessary assumption concerns the atomic orbitals at each bismuth atom that are effective in bonding. For a good, first-order representation it seems quite reasonable to consider only the three 6p orbitals as important, with the two electrons in the 6s orbital being substantially "hard-core" and nonbonding. In this case the structure is electron-deficient in that there are 27 6p AO's and 22 electrons to be accommodated in molecular orbitals.

A number of observations suggest that bonding through *n*p valence orbitals, with minimal *n*s (and *n*d) contributions, perhaps may be fairly general for compounds of elements in this region of the periodic table in which the ns^2 electrons are retained. These include the "inertness" of the s-pair so evident at and near mercury,[6] and indications of substantially p-only bonding in covalent compounds of tin(II) and lead(II),[7] TeX_6^{2-},[8] and, more distantly, in polyiodides, interhalogens,[9] and xenon fluorides.[10,11] Direct evidence for a relatively large separation between the 6p and the 6s (and 6d) level in bismuth, and hence probably limited contributions of the latter to bonding, is available in spectroscopic data.[12] In Bi^+, for example (complete data are not available for the element), the lowest state involving promotion to sp^3 (^5S) is 9.5 e.v. above ground, while the excitation to the lowest $s^2p^1d^1$ state (^3D) is 10 e.v.[13] These compare to s–p and p–d separations of 11 and 10 e.v., respectively, similarly estimated for Xe, where s and d contributions to bonding (in a somewhat different situation) are thought to be small.[11]

Symmetry Orbitals.—In the D_{3h} point group the

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[1] Presented at the 148th National Meeting of The American Chemical Society, Chicago, Ill., Aug. 30–Sept. 4, 1964. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] Deceased October 9, 1963.

[3] A. Hershaft and J. D. Corbett, *Inorg. Chem.*, **2**, 979 (1963).

[4] J. D. Corbett, *J. Am. Chem. Soc.*, **80**, 4757 (1958).

[5] *E.g.*, E. B. Moore, Jr., L. L. Lohr, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **35**, 1329 (1961).

[6] J. D. Corbett, *Inorg. Chem.*, **1**, 700 (1962).

[7] R. E. Rundle and D. H. Olson, *ibid.*, **3**, 596 (1964).

[8] D. Nakamura, K. Ito, and M. Kubo, *J. Am. Chem. Soc.*, **84**, 163 (1962).

[9] R. E. Rundle, *Record Chem. Progr.*, **23**, 195 (1962).

[10] R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 112 (1963).

[11] C. A. Coulson, *J. Chem. Soc.*, 1442 (1964).

[12] C. E. Moore, "Atomic Energy Levels," Vol. III, Circular No. 467, National Bureau of Standards, 1958.

[13] The separation increases markedly from Tl or Sb to Bi; compare the lowest excitation observed that involves s → p promotion either for s^2p configurations ($^2P \rightarrow {}^4P$): Tl, 5.6; Sn^+, 5.8; Pb^+, 7.2; Sb^{2+}, 6.7; Bi^{2+}, 8.7 e.v.; or for the unipositive ions; Tl^+, 6.4; Sn^+, 5.8; Pb^+, 7.2; Sb^+ (^3D), 8.2; Bi^+ (^3D), 11.7; (^5S), 9.5 e.v.[12]

simplest (but not the only) coordinate system for the p orbitals is with p_z at each atom vertical and parallel to C_3, Fig. 1, and the other two orthogonal orbitals in or parallel to σ_h with one directed radially or inward toward the center of the triangle of atoms and the other tangential to the figure. Hereafter these will be designated as the z, radial r, and tangential t orbital sets, since they do not mix under the operations of the group. Similarly, the six atoms that comprise the trigonal prism, 1–6, do not interchange with the three atoms 7, 8, 9 outside the faces on any symmetry operation, so that the atomic orbitals on these two types of atoms can also be considered separately. Hereafter these will be designated as terminal t and waist w atoms, respectively. There are now six independent types of orbitals to be considered, the waist zw, rw, tw, and the terminal zt, rt, tt. By standard methods of group theory,[14] these resolve into the following irreducible representations

zw: A_2'', E''
tw: A_2', E'
rw: A_1', E'
zt: A_1', A_2'', E', E''
tt: A_1'', A_2', E', E''
rt: A_1', A_2'', E', E''

So as to visualize these symmetry orbitals in subsequent treatment and discussion they are illustrated in Fig. 2 under the various representations and labeled θ_1 to θ_{27}. The signs and coefficients of the AO's in each are apparent from the figure.

It should be noted that the correct combination of the symmetry orbitals in each representation requires that each have the same transformation properties (matrices) for the operations of the group. This in effect specifies that the waist and terminal orbitals in E' and E'', Fig. 2, combine so that the AO's with coefficient two all lie on the same σ_v plane, as shown, and that, in E' for example, one of the degenerate orbitals will result from the combination of θ_6, θ_8, θ_{12}, θ_{19}, and θ_{24}.

At this point the numerical solution for approximate molecular orbitals has been reduced to solving one determinant each of order 1 × 1, 2 × 2, 4 × 4, and 5 × 5, and two of order 3 × 3. It is interesting to pause at this point so as to see what qualitative predictions might be made from inspection of the symmetry orbitals in their various representations. It is evident that five good bonding orbitals will to a large degree be constituted as A_1', θ_7–θ_{10}, θ_{22}; A_2', θ_4–θ_{17}; and A_2'', θ_1–θ_{11}, θ_{23}. The combinations in the E representations are not so obvious. However, the six additional orbitals needed for the best possible solution might be taken as those in which substantial contributions are made by $\theta_6 + \theta_{19}$ and θ_8–θ_{24} in E' and $\theta_2 + \theta_{14}$ in E''. In fact, the latter choices turn out to be correct in number but substantially incorrect in the identity of the most important contributions to the bonding. In part this is because overlap between waist and terminal sets of either z or tangential AO's involves substantial π^* contributions.

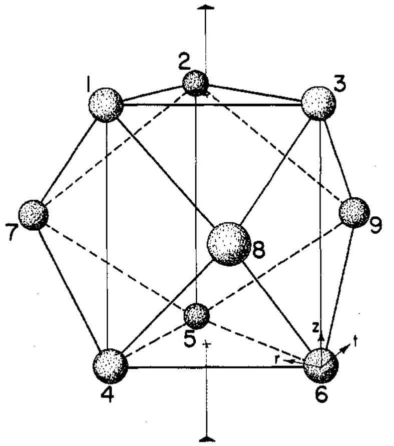

Fig. 1.—The geometry of Bi_9^{5+} and the coordinate system used.

TABLE I

OVERLAP INTEGRALS FOR SYMMETRY ORBITALS IN Bi_9^{5+} [a]

i	j	S_{ij}	i	j	S_{ij}	i	j	S_{ij}
1	1	3.101	19	19	5.439	6	12	−2.369
2	2	5.899	21	21	4.588	6	19	0.652
4	4	2.747	22	22	11.066	6	24	−1.469
6	6	2.084	23	23	9.926	8	12	2 771
7	7	3.554	24	24	8.644	8	19	1.583
8	8	5.446	26	26	6.360	8	24	−1.830
10	10	10 236	7	10	−2.771	19	24	−1.378
11	11	5.988	7	22	1.830	2	14	0.430
12	12	14.136	4	17	−1.957	2	21	3.632
14	14	5.640	1	11	−0.430	2	26	−0.637
16	16	2.524	1	23	0.637	21	26	−1.378
17	17	3.664	6	8	−0.261			

[a] Except for those in the alternate E' and E'' MO's all other overlap integrals are zero

Molecular Orbital Calculations

For LCAO molecular orbitals $\Psi = \sum_m c_i\theta_i$, the standard treatment including overlap results in m equations of the form[15]

$$c_i(\alpha_i - E) + \sum_j{}' c_j(\beta_{ij} - S_{ij}E) = 0$$

where α_i is the usual Coulomb integral H_{ii}, β_{ij}, the resonance integral H_{ij}, and S_{ij}, the overlap integral, all for normalized symmetry orbitals $N_i\theta_i$. Since overlap is significant and to be included in the symmetry suborbitals as well the normalization of $\theta_i = \sum_t a_u\Phi_u$ is $N_i^{-2} = s_i + S_{ii}$ for normalized AO's Φ_u, where $s = \sum_t a_u^2$, and S is the sum of $a_u a_{u'} S_{uu'}$ terms, *i.e.*, the total overlap within θ_i. Similarly, α_i can be separated into core terms $s_i\alpha_i'$ and the resonance integral β_{ii} between the constituent AO's. With the common assumptions that all $\beta_{ij} = S_{ij}\beta_0$ and $\alpha_i' = \alpha$, the secular equations become

$$c_i[\alpha - E + S_{ii}N_i^2(\beta_0 - \alpha)] + \sum_j{}' c_jN_iN_jS_{ij}(\beta_0 - E) = 0$$

These reduce to

$$c_i(1 - s_iN_i^2y) + \sum_j{}' c_jN_iN_jS_{ij} = 0$$

the roots of which are related to energy by $E = \alpha + (1 - y^{-1})(\beta_0 - \alpha) = \alpha + x(\beta_0 - \alpha)$.

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[14] F. A. Cotton, "Chemical Applications of Group Theory," Interscience Publishers, New York, N. Y., 1963.

[15] R. Daudel, R. Lefebvre, and C. Moser, "Quantum Chemistry, Methods and Applications," Interscience Publishers, New York, N. Y., 1959, Chapter 4.

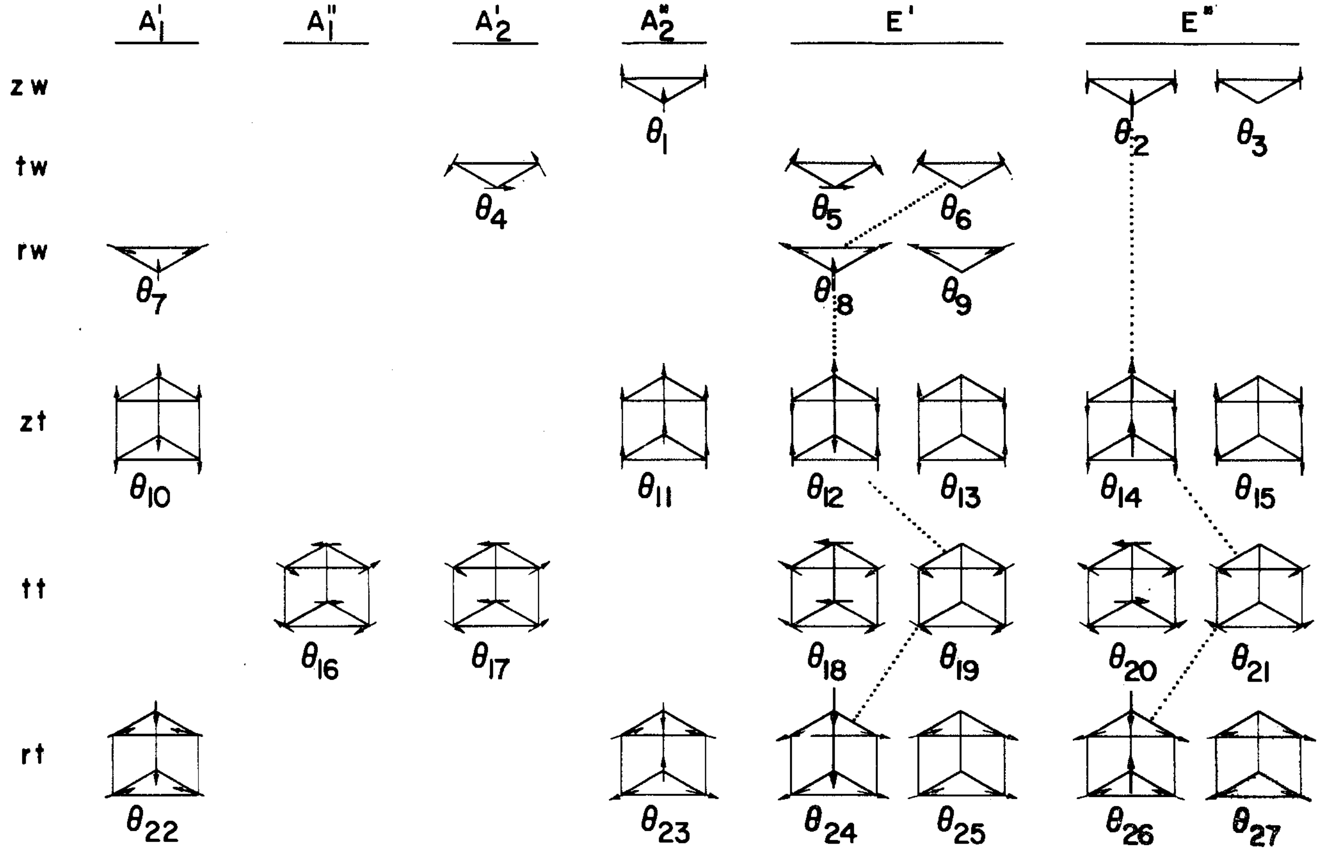

Fig. 2.—D_{3h} symmetry orbitals for Bi_9^{5+}.

The 6pσ–6pσ and 6pπ–6pπ overlap integrals were computed in terms of the parameter $p = \zeta r$ for a Slater-type orbital with the radial form $r^5 \exp(-\zeta r)$, a procedure that has been found satisfactory for 4p orbitals.[16] The value of ζ (1.84) was fixed so as to give this orbital the same $r_{\max}$ as the real Slater orbital with nonintegral exponent and a weighted value of $Z - S$ appropriate to Bi_9^{5+}. The overlap in and between symmetry orbitals i and j was calculated from the chosen figure dimensions according to $S_{ij} = k(S_\sigma \cos \phi_i \cos \phi_j + S_\pi \sin \phi_i \sin \phi_j \cos \gamma_{ij})$, where ϕ is the angle the AO's in each make with the line joining ui and uj, γ, the dihedral angle, and k, the number of times the equivalent interaction is to be counted. Nearest neighbor overlap was included within waist orbitals and between symmetry orbitals, while the second neighbor interaction was also important within the terminal θ_{10} to θ_{27}. The overlap integrals are tabulated in Table I.

Results

The normalized, one-electron molecular orbitals obtained are listed in Table II as a function of energy; the coefficients given include the normalization constant for θ_i. As is seen, there are bonding orbitals for just the 22 6p electrons in Bi_9^{5+}, $A_1'(2)$, A_2', $A_2''(2)$, $E'(2)$, and E''. This scheme also properly accounts for the diamagnetism of the ion, assuming, of course, that the 0.20 $(\beta_0 - \alpha)$ separation of bonding and nonbonding levels can be considered as "large." It should also be noted that the levels particularly in question are both A_2'', so that a more nearly exact treatment would be expected to increase their separation. Moreover, these two A_2'' levels continue to define the important bonding–antibonding gap on reasonable variations in the parameter ζ. In this case the energies of the two A_2'' orbitals as well as those of the neighboring E', A_2' *vs.* the E'* MO diverge slowly and in a parallel manner as ζ is varied from 1.70 to 2.22. For example, the $A_2'' - A_2''^*$ and the $A_2' - E'^*$ separations are 0.30 and 0.51$(\beta_0 - \alpha)$, respectively, at $\zeta = 2.0$, with about three-fourths of the changes occurring in the antibonding levels. This range for ζ corresponds to a variation in S_σ at the shortest, most frequent bonding distance (3.09 Å.) from inside the overlap maximum to a 25% lower value, with a parallel 2.7-fold decrease in S_π.

The foregoing conclusions regarding the bonding in Bi_9^{5+} might be somewhat less obvious if calculations had been made only with the frequently utilized assumption that $S_{ij} = 0$. The values of x given in parentheses in Table II are from such a zero-overlap treatment, but still retaining the relationship that $\beta_{ij} = S_{ij}\beta_0$ so that now $E = \alpha + x\beta_0$. The most striking effect is that what was formerly the lowest antibonding E' level is now apparently bonding, so that the bonding MO's are no longer closed-shell, and any agreement with the known diamagnetic property of the cation would be rather unlikely without a substantial alteration of its charge. However, this discrepancy is prob-

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[16] J. W. Richardson, private communication.

TABLE II
MOLECULAR ORBITALS FOR Bi_9^{5+}
$E = \alpha + x(\beta_0 - \alpha)$

	x		
A_2'	−2.607	(−0.723)[a]	$0.622\theta_4 + 0.609\theta_{17}$
E″	−2.508	(−0.797)	$0.510\theta_2 - 0.099\theta_{14} - 0.606\theta_{21} - 0.173\theta_{26};\ 0.883\theta_3 - 0.171\theta_{15} + 0.350\theta_{20} - 0.300\theta_{27}$
E′	−1.457	(−0.674)	$0.652\theta_6 + 0.190\theta_8 + 0.110\theta_{12} - 0.075\theta_{19} + 0.319\theta_{24};\ -0.377\theta_5 + 0.327\theta_9 + 0.191\theta_{13} + 0.044\theta_{18} + 0.553\theta_{25}$
A_1''	−1.378	(−0.579)	$0.630\theta_{16}$
E″	−1.127	(−0.530)	$-0.002\theta_2 - 0.396\theta_{14} + 0.073\theta_{21} + 0.137\theta_{26};\ -0.004\theta_3 - 0.686\theta_{15} - 0.042\theta_{20} + 0.237\theta_{27}$
E″	−0.876	(−0.363)	$0.200\theta_2 + 0.113\theta_{14} - 0.101\theta_{21} + 0.347\theta_{26};\ 0.346\theta_3 + 0.196\theta_{15} + 0.058\theta_{20} + 0.600\theta_{27}$
E′	−0.838	(−0.551)	$-0.300\theta_6 + 0.389\theta_8 - 0.235\theta_{12} - 0.104\theta_{19} + 0.060\theta_{24};\ 0.173\theta_5 + 0.673\theta_9 - 0.407\theta_{13} + 0.060\theta_{18} + 0.104\theta_{25}$
A_1'	−0.579	(−0.365)	$0.593\theta_7 + 0.255\theta_{10} - 0.149\theta_{22}$
E′	−0.211	(+0.136)	$0.286\theta_6 + 0.148\theta_8 + 0.063\theta_{12} - 0.328\theta_{19} - 0.189\theta_{24};\ -0.165\theta_5 + 0.257\theta_9 + 0.109\theta_{13} + 0.189\theta_{18} - 0.328\theta_{25}$
A_2''	−0.112	(−0.100)	$0.420\theta_1 + 0.306\theta_{11} - 0.059\theta_{23}$
	0.0	(0.0)	
A_2''	0.089	(0.098)	$-0.379\theta_1 + 0.274\theta_{11} + 0.072\theta_{23}$
A_2'	0.199	(0.249)	$-0.419\theta_4 + 0.214\theta_{17}$
E′	0.396	(0.587)	$-0.054\theta_6 + 0.176\theta_8 + 0.107\theta_{12} + 0.244\theta_{19} - 0.052\theta_{24};\ 0.031\theta_5 + 0.306\theta_9 + 0.186\theta_{13} - 0.141\theta_{18} - 0.089\theta_{25}$
A_2''	0.408	(0.690)	$0.101\theta_1 - 0.010\theta_{11} + 0.306\theta_{23}$
E′	0.430	(0.687)	$-0.342\theta_6 + 0.010\theta_8 + 0.122\theta_{12} - 0.170\theta_{19} + 0.058\theta_{24};\ 0.198\theta_5 + 0.018\theta_9 + 0.211\theta_{13} + 0.098\theta_{18} + 0.100\theta_{25}$
A_1'	0.444	(0.798)	$-0.036\theta_7 + 0.183\theta_{10} + 0.242\theta_{22}$
E″	0.457	(0.819)	$-0.197\theta_2 - 0.005\theta_{14} - 0.273\theta_{21} + 0.032\theta_{26};\ -0.341\theta_3 - 0.009\theta_{15} + 0.158\theta_{20} + 0.055\theta_{27}$
A_1'	0.566	(1.566)	$0.217\theta_7 - 0.168\theta_{10} + 0.144\theta_{22}$

[a] Without overlap; $E = \alpha + x\beta_0$.

TABLE III

	zw	tw	rw	zt	tt	rt
zw	1.854 + 0.015	0	0	0.092	0.781	0.021
tw	0	2.013 − 0.048	0.014	0.449	0.470	0.101
rw	0	0.014	1.040 − 0.015	0.449	0.262	0.144
zt	0.092	0.449	0.449	2.905 + 0.745	0	0
tt	0.781	0.470	0.262	0	3.153 + 0.470	0.172
rt	0.021	0.101	0.144	0	0.172	2.473 + 1.474
g.a.p.	2.763	2 999	1.894	4.640	5.308	4.385

ably not this serious, since the E′ level is quite sensitive to ζ in the zero-overlap approximation and, in fact, becomes approximately nonbonding ($x = 0.029$) when ζ is increased by 12%.

Discussion

By nature the occupancy and general bonding efficiency of the z, t, and r orbitals at the waist and terminal sites would be expected to be quite different in the complete picture. The distribution of bonding and of charge are described approximately by the following population matrix, $[2S_{ij}\Sigma c_i c_j]$,[17,18] where the summation is over all of the occupied MO's. In this, the diagonal terms, split so as to distinguish atomic terms from overlap within the symmetry orbitals, can be qualitatively related to the electron densities on the atoms, while the off-diagonal terms give a measure of total bond order, and the sum of a given column, the gross atomic population (g.a.p.), or, n − g.a.p., the formal charge for n AO's (Table III).

Inspection of the bond order terms for the waist atoms reveals that these are most strongly bonding to the others through tw, largely to tt (A_2') and zt (E′(1)), and, in contrast, the rw orbitals are used the least in bonding. Among the terminal orbitals self-bonding is substantial, and sources of bonding to waist atoms can be diagnosed similarly. The net result, evident in either n − g.a.p. or in the parallel (n − diagonal) terms, is that the waist orbitals by these approximations are more occupied and therefore carry less of the cationic charge, 9.00 − Σ g.a.p. = 1.34 *vs.* $5(^3/_9) = 1.67$ for uniform distribution, while the terminal atoms have a corresponding excess of the positive charge. An uneven distribution of this within either the waist or terminal sets is evident from the data. The sum of the bond orders between terminal orbitals (self-bonding) is, however, about the same as between waist and terminal sets.

The type of molecular orbital calculation that has been applied is well known to possess a number of deficiencies in the practical approximations that are required, and one which is certainly relevant here is the neglect of electron repulsions in considering the bonding in terms of a collection of one-electron MO solutions. Consequently any further refinement should obviously include both self-consistent field solutions which would account for some natural charge flow to the less occupied orbitals and the use of a range of α_i values so that the

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(17) P. O. Löwdin, *J. Chem. Phys.*, **18**, 365 (1950).
(18) W. C. Hamilton, *Proc. Roy. Soc.* (London), **A235**, 395 (1956).

more negative values would apply to the less shielded cores. The presumed minor importance of the 6s orbitals in the bonding would also be worthy of quantitative investigation. Such refinements would, of course, substantially increase the size of the problem, and they would be expected to result in only relatively small changes in the energies so that the essence of the present conclusions regarding the structure would remain unaltered.

The Bi_9^{5+} species is evidently the first example of a homopolyatomic cation of a metallic element that is sufficiently stable to exist in a pure state, excepting, of course, the diatomic Hg_2^{2+} and Cd_2^{2+}. It is interesting to note that this grouping may not be without analogy, however, since it is isoelectronic with Pb_9^{4-} and Sn_9^{4-}, two (of many) species of the post-transition metals for which Zintl and co-workers[19] found evidence in liquid ammonia. This relationship has also been noted by Britton.[20] On the other hand, no evidence for a bismuth analog of Pb_7^{4-}, the other lead anion suggested by Zintl's work, has been found in the $BiCl_3$–Bi system. In addition there is no evidence for any comparable, polynuclear cation of antimony in the SbX_3–Sb system,[21,22] perhaps due to its reluctance to form cations in the presence of halide. Compositions corresponding to the many species suggested by Zintl are generally not found in the binary alloy systems although a few isolated examples of other homopolyatomic ions with "closed-shell" MO's may occur in the latter.[23] Continued investigations may well disclose other examples of such ions for the post-transition elements that are commonly thought of as metallic in character.

Acknowledgments.—J. D. C. is particularly indebted to J. W. Richardson for the overlap computations and to D. S. Martin, Jr., for helpful discussions.

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[19] Summarized by H. J. Emeléus and J. S. Anderson in "Modern Aspects of Inorganic Chemistry," 3rd Ed., D. Van Nostrand Co., New York, N. Y., 1960, p. 512.

[20] D. Britton, *Inorg. Chem.*, **3**, 305 (1964).

[21] J. D. Corbett, S. von Winbush, and F. C. Albers, *J. Am. Chem. Soc.*, **79**, 3020 (1957).

[22] J. D. Corbett and F. C. Albers, *ibid.*, **82**, 533 (1960).

[23] J. D. Corbett, to be published.

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The Crystal Structure of Sodium Perxenate Octahydrate[1]

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Sodium perxenate octahydrate, $Na_4XeO_6 \cdot 8H_2O$, is orthorhombic with cell constants $a = 11.86$, $b = 10.36$, $c = 10.43$ Å., space group Pbcn, $Z = 4$. A three-dimensional X-ray diffraction investigation has resulted in a complete structure determination. The perxenate ion is approximately a regular octahedron with a mean Xe–O distance of 1.864 ± 0.012 Å. The greatest deviation of an O–Xe–O angle from the ideal 90° is $2.6 \pm 0.8°$. The two crystallographically independent sodium atoms are surrounded by very distorted octahedra composed of water molecules and perxenate oxygen atoms. A complex array of hydrogen bonds completes the structure.

Introduction

The reaction of XeF_6 with sodium hydroxide was shown by Malm, *et al.*,[2] to produce compounds which contain octavalent xenon and which, on the basis of chemical analyses, were thought to contain the perxenate ion, XeO_6^{-4}. In a previous communication[3] we sketched the evidence from an X-ray study that one of the compounds that forms is sodium perxenate octahydrate. Subsequent to that study Zalkin, *et al.*,[4] have shown that another product is sodium perxenate hexahydrate. In this paper we present in detail the results of our crystallographic study of sodium perxenate octahydrate and also discuss the geometry of the perxenate ion and the complex hydrogen bonding scheme in the octahydrate.

Experimental

The material studied here was prepared by adding about 1 ml. of 1 *M* NaOH to several mg. of XeF_6 at 77°K. The XeF_6 was almost certainly contaminated with XeF_4. A yellow color appeared in the frozen mixture and disappeared as the mixture melted. Colorless, well-developed crystals with dimensions of up to several tenths of a mm. formed within several minutes in the reaction vessel. Several of these crystals were selected for X-ray photography and were sealed in thin-walled glass capillaries to reduce dehydration or possible decomposition.

All photographs were taken with Mo $K\alpha$ X-rays from plate-like crystals with approximate dimensions $0.2 \times 0.2 \times 0.05$ mm. Data suitable for structure analysis were collected at room temperature by multiple-film Weissenberg photography. In order to minimize the time required to collect a complete data set, three crystals were photographed simultaneously on different cameras to obtain data from the reciprocal nets $0kl$, $1kl$, . . .$13kl$. All independent intensities strong enough to be observed and accessible within the scattering angle $\theta_{Mo} \leq 26°$ were estimated vis-

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[1] Research carried out under the auspices of the U. S. Atomic Energy Commission.

[2] J. G. Malm, B. D. Holt, and R. W. Bane, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p. 167.

[3] W. C. Hamilton, J. A. Ibers, and D. R. MacKenzie, *Science*, **141**, 532 (1963).

[4] A. Zalkin, J. D. Forrester, D. H. Templeton, S. M. Williamson, and C. W. Koch, *ibid.*, **142**, 561 (1963); A. Zalkin, J. D. Forrester, and D. H. Templeton, *Inorg. Chem.*, **3**, 1417 (1964).