The Structure of the Se_4^{2+} Ion

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THE correlation of the shapes of X_4 molecules with the number of valence electrons is possible if it is assumed that the presence of a closed-shell electron configuration is a necessary condition for stability, and that the symmetries of the occupied molecular orbitals can be determined on the basis of *s*- and *p*-orbitals alone. The *d*-atomic orbital contribution may be significant, but probably plays a secondary role in determining the geometry·

Three possible limiting geometries, linear, square-planar, and tetrahedral are considered. The symmetries for the molecular orbitals for these three shapes are

(i) Linear $D_{\infty h} = 4\sigma_u + 4\sigma_g + 2\pi_u + 2\pi_g$

(ii) Square-planar $D_{4h} = 2a_{1g} + a_{2g} + 2b_{1g} + b_{2g} + 3e_u + a_{2u} + b_{2u} + e_g$

(iii) Tetrahedral $T_d = 2a_1 + 3t_2 + t_1 + e$

If it is assumed that the σ and lone-pair orbitals are largely localized, the symmetries of the occupied orbitals may be determined using the method of Hall.[1] These are

$D_{\infty h}$
$\Gamma_\sigma = 2\sigma_g + \sigma_u$
$\Gamma_\pi = \pi_g + \pi_u$
$\Gamma_{\text{lone pair}} = \sigma_u + \sigma_g$

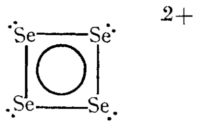
D_{4h}
$\Gamma_\sigma = a_{1g} + b_{2g} + e_u$
$\Gamma_\pi = a_{2u} + e_g$
$\Gamma_{\text{lone pair}} = a_{1g} + b_{1g} + e_u$

T_d
$\Gamma_\sigma = a_1 + e + t_2$
$\Gamma_{\text{lone pair}} = a_1 + t_2$

The order of the levels within these sets will depend on the nature of X, and could only be determined by calculations on specific molecules. However, it is only necessary to determine the symmetry of the highest orbital for each geometry. In the case of the linear and square planar molecules, elementary Hückel theory is sufficient to show that the highest orbitals are both π in character, and of symmetry π_g and e_g respectively. The highest of these levels in the tetrahedral molecule is probably one of the two t_2 orbitals, as these have some antibonding character. The application of the closed-shell criterion shows that a stable tetrahedral molecule can have a maximum of 20 valence electrons. Similarly, a stable square-planar molecule may have either 18 or 22 valence electrons, and a stable linear molecule a maximum of 18 valence electrons. Thus the theory suggests, in agreement with experiment, that P_4, with 20 electrons, will be tetrahedral, and predicts that Se_4^{2+}, with 22 electrons, will be square planar.

It has recently been shown that the Se_4^{2+} ion is stable and can be obtained by oxidation of selenium in 100% H_2SO_4, oleum, or fluorosulphuric acid.[2] Several crystalline compounds of this ion have been prepared and one of them, obtained from oleum solution, has the composition $\mathrm{Se_4(HS_2O_7)_2}$.[3] Spectroscopic studies show that it contains the $\mathrm{Se_4^{2+}}$ ion.[4] X-Ray diffraction studies gave the following results: $\mathrm{Se_4(HS_2O_7)_2}$, $M = 661{\cdot}1$, monoclinic, $a = 7{\cdot}66$, $b = 5{\cdot}90$, $c = 17{\cdot}10$ Å, $\beta = 108{\cdot}8°$, $U = 731{\cdot}6$ Å^3, $D_m = 3{\cdot}00 \pm 0{\cdot}15$, $Z = 2$, $D_c = 3{\cdot}05$, absorption coefficient $\mu = 190{\cdot}8$ cm.$^{-1}$ for Cu-K_α radiation. Space group $P2_1/c$ (C_{2h}^5). Preliminary intensity measurements for 102 $h0l$ reflections were obtained from integrating Weissenberg photographs and, despite considerable absorption effects, they were used to calculate a Patterson projection from which the x and z co-ordinates of the selenium and sulphur atoms were obtained. Calculations of the electron-density projection using these co-ordinates enabled the positions of most of the oxygen atoms to be found. After Fourier and least-squares refinement, the agreement index, R, was reduced to 0·19. Although further refinement must await the collection of better data the grouping of the four selenium atoms is clear. Viewed down the b-axis, they form a parallelogram around either a screw axis or a centre of symmetry. Since a screw axis is incompatible with a discrete tetramer, $\mathrm{Se_4^{2+}}$ must possess a centre of symmetry and hence be planar. If one assumes that the selenium atoms lie at the corners of a square, the Se–Se distance is close to 2·28 Å. The presumably single-bond distance in $\mathrm{Se_8}$ is 2·34 Å.[5]

The structure of the $\mathrm{Se_4^{2+}}$ ion may be written as



where the circle denotes a closed-shell ("aromatic") six π-electron system. According to simple Huckel theory the π-bond order of each bond is 0·5 which is consistent with the observed bond length. The intense yellow-orange colour of the $\mathrm{Se_4^{2+}}$ ion ($\lambda_{\max} = 410$ nm., $\epsilon = 8000$)[2] is also explained in terms of Hückel theory. A low-lying excited state is to be expected from the dipole-allowed excitation of an electron from the highest filled π-orbital, which **is** of symmetry e_g and almost nonbonding, to the lowest empty π-orbital (b_{2u}).

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