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THE MOLECULAR STRUCTURES OF COMPOUNDS OF RARE-GAS ELEMENTS

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Since the preparations of xenon fluorides were reported¹⁾, the molecular structures of these compounds have been studied²⁾ and theoretical interpretation of the chemical bonding involved has been attempted³⁾. The present communication reports that the structures of these unusual compounds may also be predicted, though qualitatively, from the more simple theory without invoking rather sophisticated theories.

It was pointed out previously by Tsuchida⁴⁾ and by Sidgwick and Powell⁵⁾ that the stereochemistry of an atom in a molecule is determined by the size of its valency shell including the lone pairs, and that the lone pairs are equally as important as the bonding pairs in this respect. Using the terminology in co-ordination chemistry, one may well say that this theory assumes, in the imaginary process of deriving the structures of the molecule, the co-ordination of ligands with the central positive ion of Kossel-type, the lone pairs being regarded as equivalent to the other ligands. The theory was improved later by Nyholm and Gillespie⁶⁾, by taking account of the differences in the electrostatic repulsions between lone pairs, between lone pairs and bonds, and between bonds themselves.

On the basis of this theory, the structures of the compounds of rare-gas elements are readily predicted as shown in Fig. 1. Thus the molecular structure of xenon trioxide, XeO_3 , is pictured as derived through co-ordination of three O^{2-} ions and one lone pair of electrons to a Xe^{8+} core. So far, the molecular structures of xenon difluoride, xenon tetrafluoride, and xenon trioxide have been determined²⁾. These are found to be in agreement with the structures predicted in the present communication. The structures of compounds of other rare-gas elements, such as KrF_4 , if prepared at all, may be predicted in the same way. Particularly interesting seems to be the predicted structure for xenon hexafluoride, which shows some distortion from regular octahedron.

It seems to be worth noting that this simple theory, which proved to be qualitatively valid in predicting the shapes of most compounds of "typical elements" and many "transition-metal elements", also applies to the compounds of rare-gases.

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Molecule or ion	Central ion	Ligands*	Co-ordination number and corresponding hybrid orbitals	Configuration
XeO_3	Xe^{8+}	3O^{2-} and $1:$	4 sp^3	Tetrahedron
XeF_2	Xe^{8+}	2F^- and $3:$	5 sp^3d	Linear
XeF_4 (KrF_4)	Xe^{8+}	4F^- and $2:$	6 sp^3d^2	Square plane
XeF_5^+	Xe^{8+}	5F^- and $1:$	6 sp^3d^2	Square pyramid
XeF_6	Xe^{8+}	6F^- and $1:$	7 sp^3d^3	

Fig. 1 Shapes of compounds of rare-gas elements
 * The symbol, :, represents a lone pair of electrons.

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