rocycle. The opening in the middle of the 16-membered TAAB ligand is too large to form strong bonds to the small vanadium(V). However, larger ions such as cobalt(II), nickel(II), and copper(II) can fit snugly inside the large TAAB ligand. On the other hand, the vanadium(V) can form a more stable compound by coordinating to the smaller 12-membered macrocycle, TRI.

Another explanation for the selectivity of TRI for VO_2^+ may be due to the cis configuration of the oxygens on VO_2^+.[14-16] These cis oxygens should make it very difficult for the cyclic tetradentate ligand TAAB to coordinate in the same plane as the vanadium(V). However, the TRI should coordinate with ease to an available face of an octahedron.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Also, support by the BGSU Faculty Research Committee is gratefully acknowledged, and we thank C. Myer for repeating some of the syntheses.

Registry No. Compound A, 56571-74-5; $[(VO)_2(TRI)_2(OH)_2]Cl_4$, 56571-75-6; $[(VO)_2(TRI)_2(OH)_2][B(C_6H_5)_4]_4$, 56488-45-0; $[(VO)_2(TRI)_2(OH)_2][HgI_4]_2$, 56488-44-9; *o*-aminobenzaldehyde, 529-23-7; $VOCl_2$, 10213-09-9; $(TAAB)(HClO_4)_2$, 56487-96-8.

References and Notes

(1) D. H. Busch, *Science*, 171 (1968).
(2) M. M. Jones, "Ligand Reactivity and Catalyses", Academic Press, New York, N.Y., 1968, Chapter 3.
(3) D. H. Busch, *Rec. Chem. Prog.*, **25**, 107 (1964).
(4) G. A. Melson and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 4834 (1964).
(5) L. F. Lindoy and D. H. Busch, *Prep. Inorg. React.*, **6** (1970).
(6) L. T. Taylor, S. C. Vergez, and D. H. Busch, *J. Am. Chem. Soc.*, **88**, 3170 (1966).
(7) S. C. Cummings and D. H. Busch, *J. Am. Chem. Soc.*, **92**, 1924 (1970).
(8) D. H. Busch and S. L. Cummings, *Inorg. Chem.*, **10**, 1220 (1971).
(9) J. Selbin, *Chem. Rev.*, **65**, 153 (1965).
(10) J. Selbin, *Coord. Chem. Rev.*, **1**, 293 (1966).
(11) S. G. McGeachin, *Can. J. Chem.*, **44**, 2323 (1966).
(12) J. Selbin and G. Vigel, *J. Inorg. Nucl. Chem.*, **10**, 1644 (1968).
(13) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry", J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N.Y. 1960, p 403.
(14) W. R. Scheidt, C. Tasi, and J. L. Hoard, *J. Am. Chem. Soc.*, **93**, 3867 (1971).
(15) W. R. Scheidt, D. M. Collins, and J. L. Hoard, *J. Am. Chem. Soc.*, **93**, 3878 (1971).
(16) W. R. Scheidt, R. Countryman, and J. L. Hoard, *J. Am. Chem. Soc.*, **93**, 3878 (1971).

Correspondence

Comments on the Application of Symmetry Ascent Selection Rules to a Factor Group Analysis of Red Mercuric Iodide

AIC50165A

Sir:

The Raman spectrum of the red modification of mercuric iodide has been the subject of several investigations. It is therefore somewhat surprising to discover that the interpretation of its vibrational spectrum is still a subject of discussion.

In recent years it has become clear that the crystallographic point group corresponding to a particular lattice is not necessarily isomorphic to the factor group most appropriate to a vibrational analysis. Lever et al. have recently attempted to place these changes in crystallographic point group, which involve ascent to a group of higher symmetry, on a more formal basis,[1] obtaining results which are very similar to those of Boyle.[2] Hollebone and Lever[3] have applied their method of ascent in symmetry to the case of the vibrational spectrum of the red crystalline modification of HgI_2. It is the purpose of the present communication to indicate our reservations concerning the validity of their approach.

Red mercuric iodide crystallizes in the $P4_2/nmc$ space group (D_{4h}^{15}). There are two molecules in the primitive unit cell. The factor group predictions together with the commonly accepted assignments of the observed bands are given in Table I.[4-8] Of particular interest is the reason for the very low frequencies observed for the two internal E_g modes and the absence of two predicted Raman-active lattice modes.

It has been suggested[3] that these observations are understandable if the mercuric iodide lattice is regarded as a distorted cubic lattice (ca. O_h^5). However, we believe that the O_h^5 lattice cannot exist, invalidating this explanation of the spectrum.

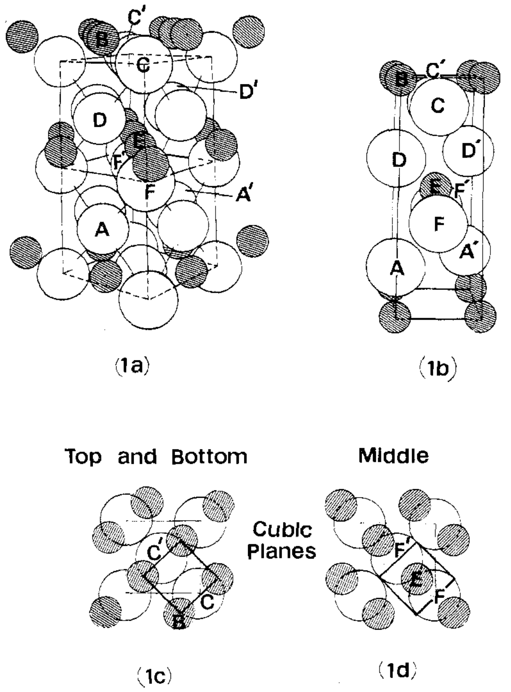
The relationship between the lattice of face-centered cubic packed iodide ions and the red mercuric iodide structure is shown in Figure 1, where the very small departure of the iodide ion packing from ideality has been ignored. While Hollebone and Lever[3] stated that they "remove the tetragonal distortion from each sublattice", in their diagram (Figure 2 of their paper) they move only iodine atoms (moving those labeled A, A', C, C', D', F, and F' in Figure 1 of the present paper). In fact, such a movement destroys the cubic arrangement of iodide ions. Indeed, the "cubic" unit cell generated by these authors has sides of relative dimensions $1:1:2^{1/2}$!

Table I

D_{4h}^{15} modes		Obsd freq, cm^{-1}	Ref
Acoustic	A_{2u}		
	E_u		
Lattice	B_{1g}	Not obsd	
	E_g	Not obsd	
Internal	A_{1g}	114	5-7
	B_{1g}	142	5, 7
	2 E_g	17, 29	5-7
	A_{2u}	112	8
	B_{2u}	Inactive	
	$2E_u$	12, 26	4

Figure 1a shows a cubic close-packed arrangement of iodide ions (the unit cell being indicated) together with the corresponding lattice of mercuric ions. Figure 1b shows the unit cell of the mercuric iodide lattice; comparison with Figure 1a demonstrates the relationship between the mercuric iodide unit cell and the face-centred cubic lattice of iodide ions. This comparison is continued in Figures 1c and 1d, which show three projections of part of the structures, onto the "top" (or "bottom") and "middle" sections of the lattices shown in Figures 1a and 1b.

The question remains as to whether any simplification of the interpretation of the mercuric iodide vibrational spectrum can be obtained by a method analogous to that used by Hollebone and Lever. The only plausable displacement seems to be that of moving the mercury ions by an amount $|a/2(2^{1/2})|$ as indicated in Figure 2. This movement has the effect of placing these ions in octahedral holes and gives a unit cell (Figure 3) containing one HgI_2 molecule. All the atoms in this lattice lie on centers of symmetry and so their cartesian displacements subtend only ungerade irreducible representations of the appropriate factor group—it is isomorphic to D_{4h} (the space group is now $P4/mmm$, D_{4h}^1). Comparison with



(1a) (1b)

(1c) (1d)

Figure 1. (a) Face-centered cubic iodide lattice. (b) Mercuric iodide unit cell. (c and d) Partial projective sections of planes of (a) and (b), the cubic unit cell being shown faint and the mercuric iodide unit cell bold. In this figure all atoms have been labeled in a similar manner to those of Figure 2 of ref 3.

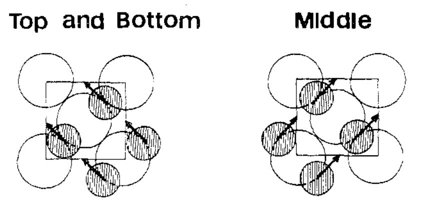


Figure 2. Displacement of mercury atoms from their positions shown in Figure 1b and c. All displacements are $a/2(2^{1/2})$.

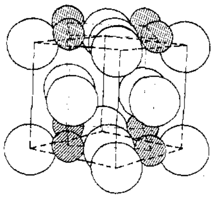


Figure 3. Unit cell of $D_{4h}{}^1$ symmetry generated by the displacements indicated in Figure 2.

the correct factor group representations (Table I) would then require that all the vibrating modes which have gerade characteristics in Table I correlate with acoustic modes in the $D_{4h}{}^1$ factor group. It follows that, on this model, all Raman-active modes of HgI_2 would be expected to have frequencies much lower than the infrared-active modes. This is not in accord with the spectral observations. We conclude that the interpretation of the vibrational spectra of HgI_2 cannot be aided by recourse to a $D_{4h}{}^1$ factor group.

There are several cubic AB_2 lattices in which the B atoms are cubic close packed and the A atoms are distributed over appropriate holes. Cuprite, Cu_2O, is one example. Anatate, TiO_2, with the tetragonal distortion removed, is another. However, their unit cells each require several AB_2 molecules in a unit cell and so do not provide a basis for a simple explanation of the vibrational spectra of HgI_2.

We conclude that there seems to be no reason for discussing the vibrational spectrum of HgI_2 in any factor group other than $D_{4h}{}^{15}$.

Acknowledgment. E.L.B. is indebted to the SRC for financial support.

Registry No. HgI_2, 7774-29-0.

References and Notes

(1) B. R. Hollebone, A. B. P. Lever, and J. C. Donini, *Mol. Phys.*, **22**, 155 (1971).
(2) L. L. Boyle, *Spectrochim. Acta, Part A*, **28**, 1347 (1972), and references therein.
(3) B. R. Hollebone and A. B. P. Lever, *Inorg. Chem.*, **11**, 1158 (1972). Note that Table I in this paper contains several errors.
(4) J. P. Mon, *C. R. Hebd. Seances Acad. Sci, Ser. B*, **262**, 493 (1966).
(5) R. P. J. Cooney, J. R. Hall, and M. A. Hooper, *Aust. J. Chem.*, **21**, 2145 (1968).
(6) A. J. Melveger, R. K. Khanna, B. R. Guscott, and E. R. Lippincott, *Inorg. Chem.*, **7**, 1630 (1968).
(7) D. M. Adams and M. A. Hooper, *Aust. J. Chem.*, **24**, 885 (1970).
(8) Y. Mikawa, R. J. Jakobseu, and J. W. Brasch, *J. Chem. Phys.*, **45**, 4528 (1966).

School of Chemical Sciences
University of East Anglia
Norwich, England NOR 88C

E. L. Burrows
S. F. A. Kettle*

Received March 4, 1975

Additions and Corrections

1975, Volume 14

Robert C. Pierce and Richard F. Porter*: Ion–Molecule Chemistry of BF_3 and HBF_2 in Hydrogen.

Pages 1087–1092. All third-order rate constants (k_3) appearing in Table III and in the text should have the units $cm^6/(molecule^2\ sec)$.