Figure 2.—Infrared spectra of KBr disks of [Re(CO)₄H]₃ (solid line) and [Re(CO)₄D]₃ (dashed line).

TABLE III

INFRARED SPECTRA OF SOLID [Re(CO)₄H]₃ AND [Re(CO)₄D]₃ IN CO STRETCHING REGION

⟶[Re(CO)₄H]₃⟶		⟶[Re(CO)₄D]₃⟶	
ν, cm.$^{-1}$	Int.^{a}	ν, cm.$^{-1}$	Int.^{a}
2095	m	2093	m
		2045	w
2030	m, sh	2030	m
		2018	m
2005	s	2000	s
1985	w, sh	1982	m
		1970	w
1962	m	1958	s

^{a} Intensities are rough estimates: s, strong; m, medium; w, weak; sh, shoulder.

cm.$^{-1}$ as a rhenium–hydrogen stretching frequency.[7] We believe this to be a vibration involving a hydrogen bridge between two rhenium atoms (Re–H–Re), as postulated previously.[4] Such an assignment is consistent with the unusually low value of the hydrogen stretching frequency and constitutes the first reported observation of a bridging hydrogen between two transition metal atoms.

In the Raman spectra of the solids, rather striking differences appear in the CO stretching region. For example, peaks at 2012 and 1954 cm.$^{-1}$ for the hydride are shifted to 2023 and 1962, cm.$^{-1}$ respectively, for the deuteride. There are other less dramatic changes also. In the infrared spectrum the shifts are somewhat less pronounced and more difficult to assign because of the number of peaks. The shifts specified above for the

(7) Unfortunately the infrared spectra showed only very weak and ill-defined absorptions in this region, even using saturated solution in 1-mm. cells and concentrated KBr pellets. Thus they offered no further support to such an assignment.

CO stretching region are too small, and in the wrong direction, for a hydrogen vibration. However, we can certainly conclude that the substitution of deuterium for hydrogen has led to definite changes in the CO stretching frequencies. Thus the hydrogen (or deuterium) is part of the molecular entity.

A reasonable explanation of the shifts in CO stretching frequencies can be offered. The Re–H stretching vibration at 1100 cm.$^{-1}$ may have an overtone, or combination with another Re–H frequency, in the 2000–2100 cm.$^{-1}$ region. This overtone or combination could then interact through Fermi resonance with nearby CO stretching vibrations of proper symmetry, depressing their frequencies. For the deuteride the analogous overtone, or combination, would be out of the CO stretching region and thus would not interact.

It is surprising that the Raman solution spectra of the hydride and deuteride do not show the differences brought out in the spectra of the solids. Thus from the three peaks reported in Table I it would be impossible to distinguish hydride from deuteride. In the infrared[4] the differences are very slight for solutions of the hydride and deuteride. Apparently the hydrogen stretching frequency interacts with the CO stretching frequencies only weakly in solution but quite strongly in the solid. This may be because the symmetry is lower in the solid than in solution, giving increased possibility of Fermi resonance.

NOTE ADDED IN PROOF.—The highest observed Raman frequency (2125 cm.$^{-1}$, strong) and the highest observed infrared frequency (2093, strong),[4] in aqueous solution, can be assigned as the $A_1{}^1$ and E^1 vibrations, derived from the axial A_1 mode of the hypothetical isolated Re(CO)₄ group.[8] A fuller analysis[9] shows that the A_1 mode is split due to interaction of carbonyl groups on different metal atoms. A similar phenomenon is found in Mn₂(CO)₁₀,[10] but the interaction is stronger in these molecules (which contain a direct metal–metal bond) than in [Re(CO)₄H]₃ (in which the metal–metal bonds are almost certainly hydrogen-bridged).

(8) Assignments were made assuming D₃ₕ symmetry. See ref. 4, Figure 1b, and related discussion in the text.

(9) P. S. Braterman, H. D. Kaesz, and J. M. Smith, to be published.

(10) F. A. Cotton and R. Wing, *Inorg. Chem.*, 4, 1328 (1965).

On the Structure of Germanium Selenide and Related Binary IV/VI Compounds

By S. N. DUTTA AND G. A. JEFFREY

It is known that certain binary compounds exhibit the structural characteristics of the elements in their

mean periodic group. This trend has been particularly well explored for the I/VII, II/VI, and III/V compounds which have four-coordinated tetrahedral arrangements characteristic of the group IV elements.

It is interesting to inquire to what extent this relationship applies to compounds whose elements are less symmetrically disposed in the periodic table. This note is concerned with a re-examination of the structure of the IV/VI compound, GeSe.

Experimental

The crystal structure of germanium selenide has been refined using 170 observed structure amplitudes obtained photographically from single crystals with Cu Kα radiation. The diffraction intensities were corrected for angle factors and absorption and the scattering factors were corrected for dispersion. Starting with the positional parameters given by Kannewurf, Kelly, and Cashman,[1] three cycles of anisotropic refinement using the full-matrix IBM 7090 program of Busing, Martin, and Levy[2] converged with significant changes only in the temperature factors. The weighting scheme used in the refinement was $w = (a + |F_o| + c|F_o|^2)^{-1}$ where $a = 2F_{min}$ and $b = 2/F_{max}$. Our structural data given in Table I therefore agree with the earlier results[1] within the limits of error, except for the thermal parameters. The final agreement index, excluding unobserved reflections, was $R = 0.11$. An estimate of the accuracy of the experimental intensities based on the consistency of values obtained from two different crystals was about 9%. The plastic nature of the crystal determined this limitation on the experimental data. The heights and curvatures of the electron density peaks of the atoms were examined by differential and difference Fourier syntheses. The germanium and selenium atoms were clearly distinguished and there was no evidence of disorder or nonstoichiometry within the limits of error of the experimental observations.

TABLE I

THE STRUCTURAL DATA FOR GeSe

Orthorhombic, $a = 4.403 \pm 0.005$ Å., $b = 3.852 \pm 0.005$ Å., $c = 10.82 \pm 0.01$ Å. $Z = 4$, $D_m = 5.49$, $D_x = 5.49$ g./cc. Space group Pcmn, from extinctions and statistical intensity distributions

	x	z	e.s.d., Å.
4 Ge in 4(c)	0.1097	0.8787	0.003
4 Se in 4(c)	0.5020	0.1467	0.003

	$\beta_{11}{}^a$	$\beta_{22}{}^a$	$\beta_{33}{}^a$	$\beta_{13}{}^a$	$\rho_{obsd},$ e/Å.³	$\rho_{obsd},$ e/Å.³
Ge	0.034	0.051	0.0055	0.0016	70.1	69.5
Se	0.029	0.037	0.0051	0.0004	82.4	81.8

The Thermal Ellipsoids[b]

	$|\overline{r_i^2}|^{1/2}$	i	g_{ia}	g_{ib}	g_{ic}
Ge	0.171	1	133.6	90.0	43.6
	0.192	2	136.4	90.0	133.6
	0.196	3	90.0	0.0	90.0
Se	0.166	1	20.4	90.0	110.4
	0.166	2	90.0	180.0	90.0
	0.176	3	69.6	90.0	20.4

[a] β_{ij} is consistent with temperature factor exponents of the form exp $-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{13} + 2k\beta_{23})$. [b] Root-mean-square displacements in Å. and directions of principal axes in degrees.

Discussion

The structure of germanium selenide can be described as a distorted NaCl structure inasmuch as each atom has six unlike atoms as its first nearest neighbors.

(1) C. R. Kannewurf, A. Kelly, and R. J. Cashman, *Acta Cryst.*, **13**, 449 (1960).

(2) W. R. Busing, K. O. Martin, and H. A. Levy, Report ORNL TM-305, Oak Ridge National Laboratory, 1962.

However, the interatomic vectors do not lie on spherical shells but are so spread that the longest Ge–Se first neighbor distance is only 0.03 Å. shorter than the shortest Ge–Ge distance. These distances are given in Table II, together with the angles which correspond to a very distorted octahedral coordination around the atoms.

TABLE II

FIRST AND SECOND NEAREST NEIGHBOR INTERATOMIC DISTANCES IN GeSe[a]

First Neighbor Distances, Å.

Ge I–Se I	3.37	Se I–Ge I	3.37
Ge I–Se II	2.56	Se I–Ge II	2.56
Ge I–Se III	3.32	Se I–Ge III	3.32
Ge I–Se$_x$ III′	2.59	Se I–Ge$_x$ III′	2.59
Ge I–Se$_{x,y}$ III″	2.59	Se I–Ge$_{x,y}$ III″	2.59
Ge I–Se$_y$ III′	3.32	Se I–Ge$_y$ III′	3.32

Second Neighbor Distances, Å.

Ge I–Ge$_x$ I′	4.40	Se I–Se$_x$ I′	4.40
Ge I–Ge$_x$ I′	4.40	Se I–Se$_x$ I′	4.40
Ge I–Ge$_y$ I′	3.85	Se I–Se$_y$ I′	3.85
Ge I–Ge$_y$ I′	3.85	Se I–Se$_y$ I′	3.85
Ge I–Ge III	3.40	Se I–Se III	5.74
Ge I–Ge$_x$ III′	4.73	Se I–Se$_x$ III′	3.71
Ge I–Ge$_{x,y}$ III″	4.73	Se I–Se$_{x,y}$ III″	3.71
Ge I–Ge$_y$ III′	3.40	Se I–Se$_y$ III′	5.74
Ge I–Ge IV	4.04	Se I–Se IV	3.68
Ge I–Ge$_x$ IV′	4.04	Se I–Se$_x$ IV′	3.68
Ge I–Ge$_{x,y}$ IV″	4.04	Se I–Se$_x$ IV″	3.68
Ge I–Ge$_y$ IV′	4.04	Se I–Se$_y$ IV′	3.68

Angles between Primary Bonds in GeAs, deg.

Se II–Ge I–Se$_x$ III′	91.3	Ge II–Se I–Ge$_x$ III′	103.3
Se II–Ge I–Se$_{x,y}$ III″	91.3	Ge II–Se I–Ge$_{x,y}$ III″	103.3
Se$_x$ III′–Ge I–Se$_{x,y}$ III′″	96.1	Ge$_x$ III′–Se I–Ge$_{x,y}$ III″	96.1

[a] The estimated standard deviations are 0.005 Å. The symmetry related positions are given by: I (x, y, z); II $(1/2 - x, 1/2 - y, 1/2 + z)$; III $(-x, 1/2 + y, -z)$; IV $(1/2 + x, -y, 1/2 - z)$. Primes indicate a single or a double unit translation in directions denoted by the subscripts.

The structure is, in fact, much closer to a 3/3 arrangement with three nearly equidistant selenium atoms bonded pyramidally at 2.56–2.59 Å. to each germanium atom with Se–Ge–Se angles of 91 to 96°. The selenium environment is similar except that the Ge–Se–Ge angles are larger, 96 to 103°. This gives rise to the double-layer structure shown in Figures 1 and 2 which is isostructural with that of black phosphorus, *cf.* Figures II. 16a and II. 16b of Wyckoff.[3] The weak bonding between adjacent double layers corresponds with the marked (001) cleavage. The extent to which certain IV/VI binary compounds have the group V stereochemistry is shown in Table III.

TABLE III

	S	Se	Te
Ge	Black P	Black P	As NaCl[a]
Sn	Black P	Black P	NaCl
Pb	NaCl	NaCl	NaCl

[a] Above 400°.

In both the arsenic and black phosphorus structures the formation of three strong primary bonds leads to

(3) W. G. Wyckoff, "Crystal Structures," Vol. 1, 2nd Ed., Interscience Publishers, New York, N. Y., 1963.
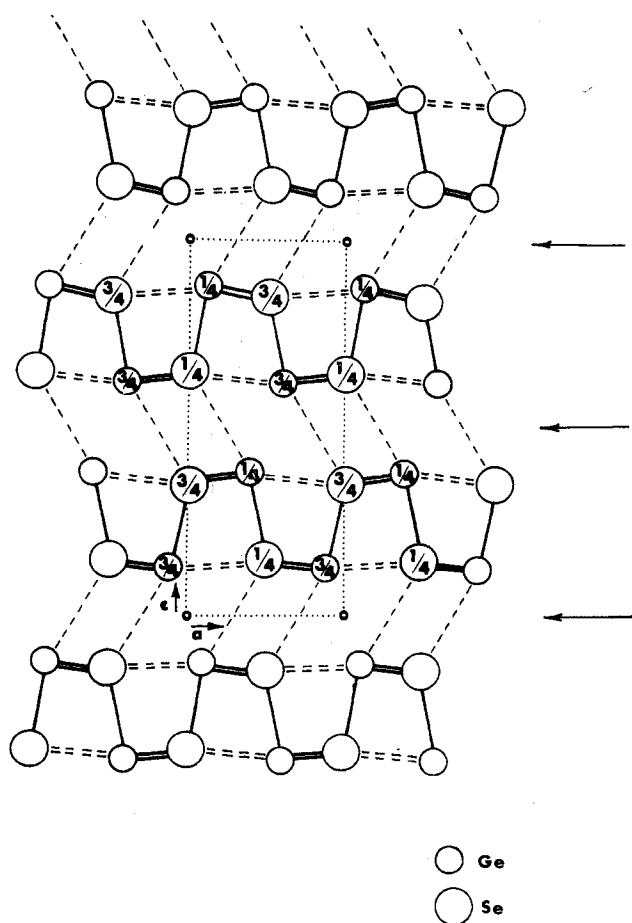
Figure 1.—Crystal structure of GeSe; view down [*b*]: ———, primary bonding; ---------, secondary bonding; ......, unit cell; ◄———, cleavage plane.
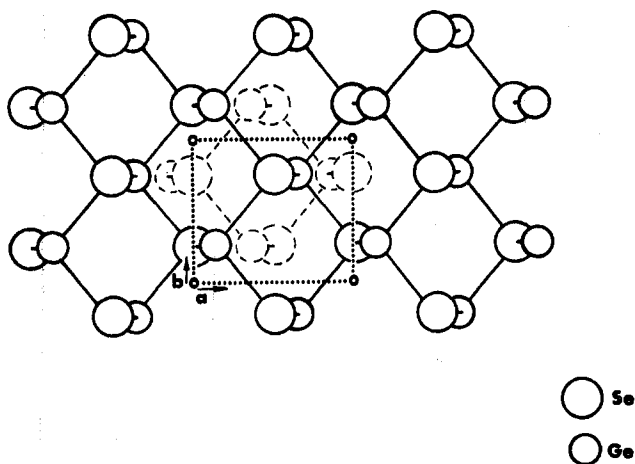

Figure 2.—Crystal structure of GeSe; view down the [*c*] axis showing two layers in the unit cell. The broken lines correspond to the lower layer. The dotted line is the unit cell.

structures which are different in a way which is illustrated in Figure 3. Clearly these two structures correspond to two possible ways of forming a puckered-layer giant molecule infinitely extending in two dimensions using a pyramidal primary-bond arrangement. In the arsenic and the low-temperature phase of GeTe[4] struc-

(4) K. Schubert and H. Fricke, *Z. Metallkunde*, **44**, 457 (1963).

tures, each atom has its three bonded neighbors in the adjacent layer of the double layer, and hence each layer is based on a hexagonal array as shown in Figure 4a. The stacking sequence of the layers is BA–CB–AC as also shown in Figure 4a. In the GeSe and black P structure, each atom has two bonded neighbors in the same layer and one in the adjacent layer. Because of the nearly 91° valence angles, this leads to a pseudo-orthogonal array in each layer. The *idealized* orthogonal array and the stacking sequence, which is AB–CD–AB, is shown in Figure 4b. This stacking arrangement is significantly less dense than that based on the hexagonal layers, *cf. d* = 5.49 g./cc. for GeSe *vs.* 5.73 g./cc. for As. But the most marked distinction is in the bonded and nonbonded layer separations. In GeSe, the mean separations A···B and B···C are 2.50 and 2.92 Å. In As, the corresponding layer separations A···C and A···B are 1.26 and 2.26 Å. In both structures the displacement of the adjacent layers is such as to minimize the nonbonding interaction of the lone pairs in the sp^3-type orbitals. In As these orbitals will extend normal to the layers and form an interleaving hexagonal array with those from adjacent nonbonding layers. The same is true in GeSe, except that the axes of the nonbonding orbitals will be inclined at an angle of approximately 45° to the mean plane of the layers.

The interatomic distances shown in Table IV for these IV/VI structures show some interesting trends in Δ, which is zero for the NaCl-type structure. In

TABLE IV

COMPARISON OF FIRST NEIGHBOR DISTANCES (Å.) IN GERMANIUM AND TIN SULFIDES AND SELENIDES[a]

Ge	1 S	2.47	Ge	1 Se	2.56	P–P = 2.18
	2 S	2.64		2 Se	2.59	Δ = 1.69
	1 S	2.91		2 Se	3.32	As–As = 2.51
	2 S	3.00		1 Se	3.37	Δ = 0.64
	Δ = 0.39			Δ = 0.77		
Sn	1 S	2.62	Sn	1 Se	2.77	Sb–Sb = 2.87
	2 S	2.68		2 Se	2.82	Δ = 0.46
	2 S	3.27		2 Se	3.35	Bi–Bi = 3.10
	1 S	3.39		1 Se	3.47	Δ = 0.36
	Δ = 0.65			Δ = 0.59		

[a] Δ is difference in Å. between the average of the three closest and the three second closest distances.

black phosphorus, where Δ = 1.69, there are three primary localized-pair bonds and very weak secondary bonding, whereas in As, Sb, and Bi the values of 0.64, 0.46, and 0.36 correspond to an increasing trend to six resonating or partly delocalized bonds which are associated with semiconducting and eventually metallic properties.[5] From the Δ values, it is obvious that although the atomic arrangement of the sulfides and selenides of germanium and tin more closely resembles that of black phosphorus, the atomic bonding is closer

(5) E. Mooser, and W. B. Pearson, "Progress in Semiconductors. V," Butterworth and Co. (Publishers) Ltd., London, 1960.
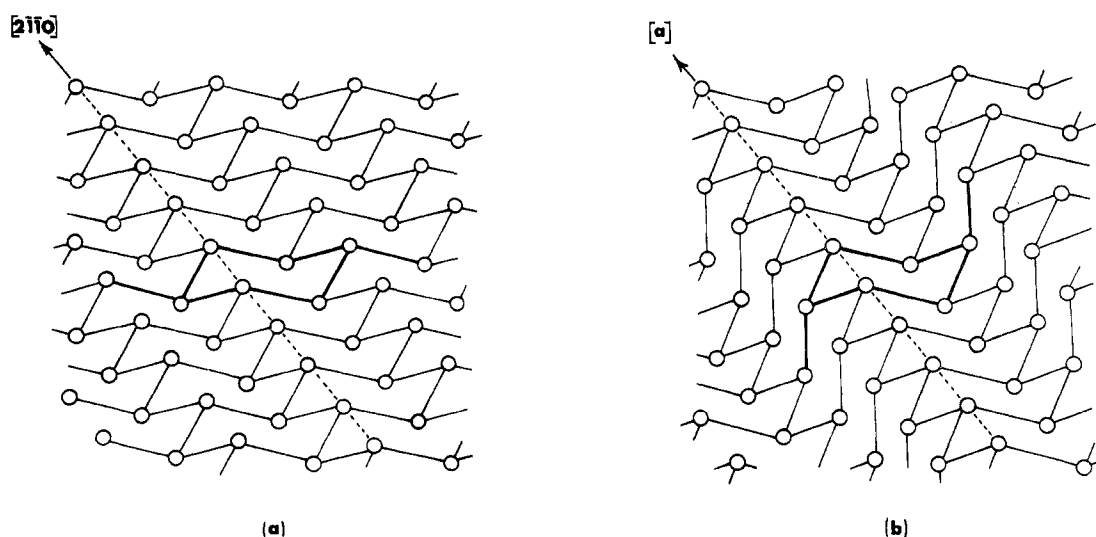
Figure 3.—(a) The double layer of primary bonded atoms in the As structure. (b) The corresponding double layer of primary bonded atoms in the black phosphorus and GeSe structures.
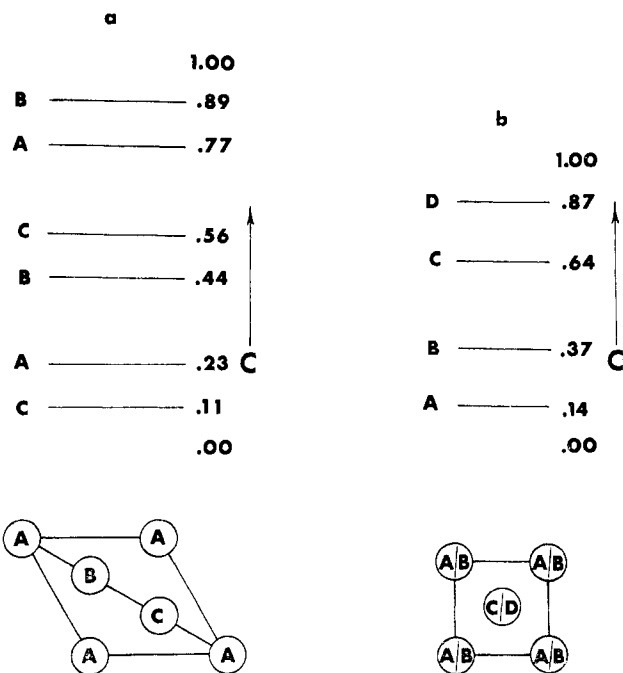

Figure 4.—Layer stacking sequences: a, arsenic structure; b, GeSe structure.

to that of arsenic and bismuth. The interatomic distances are very similar, both with respect to first neighbor coordination and the difference between first and second neighbor distances, and this is in agreement with the semimetallic character of these materials. It is not at all obvious, however, why these binary compounds have the black phosphorus rather than the arsenic structure, which is equally compatible with these first and second neighbor interactions and would permit a higher density of atomic packing.
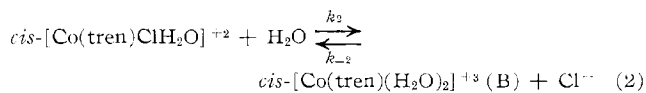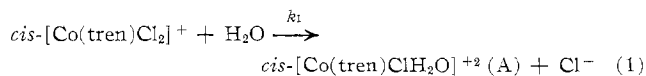
Substitution Reactions of *cis*-Dichloro(β,β',β''-triaminotriethylamine)cobalt(III) Complex Ion. Kinetics of Aquation of *cis*-Dichloro-(triaminotriethylamine)cobalt(III) Ion[1]

BY STANLEY K. MADAN,[2] WILLIAM M. REIFF,
AND JOHN C. BAILAR, JR.

The object of this study was to gain information regarding the kinetics of the aquation of *cis*-dichloro(triaminotriethylamine)cobalt(III) chloride, in which the steric property of the molecule is fixed, since the tertiary nitrogen atom must be *trans* to a chloro group. It has been found that the controlled configuration has a striking effect on the reaction rate under various conditions.

The aquation reaction, which has been conducted in 0.1 M acid solution, takes place in two steps, which may be written as

$$\textit{cis-}[Co(tren)Cl_2]^+ + H_2O \xrightarrow{k_1}$$
$$\textit{cis-}[Co(tren)ClH_2O]^{+2} (A) + Cl^- \quad (1)$$

$$\textit{cis-}[Co(tren)ClH_2O]^{+2} + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}$$
$$\textit{cis-}[Co(tren)(H_2O)_2]^{+3} (B) + Cl^- \quad (2)$$

The kinetic measurements made in this study may also be cited as support for the stepwise aquation, even though salts containing ion A have never been isolated. Reaction 1 proceeds at a much greater rate than reaction 2, so that no serious interference is caused

(1) This article is based upon part of a dissertation submitted by S. K. Madan in partial fulfillment of the requirements for the Ph.D. degree at the University of Illinois, 1960.

(2) Socony-Mobil Research Assistant, University of Illinois, 1956–1957.