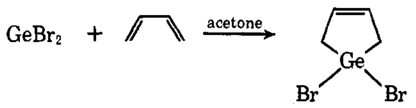
Cl bond of germanium tetrachloride, followed by halogen exchange with excess tetrachloride, would be a desirable route to large quantities of hexachlorodigermane. However, under conditions employed for the preparation of Ge_2Br_6, the dibromide failed to react with germanium tetrachloride. Germanium dibromide also did not react with the methylbromogermanes, $(CH_3)_nGeBr_{4-n}$. The dibromide does react with carbon tetrabromide, however, to form tribromomethyltribromogermane (I)

$$GeBr_2 + CBr_4 \longrightarrow \underset{I}{Br_3C\text{–}GeBr_3} \qquad (4)$$

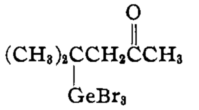
Compound I is a white, air-stable solid which melts with decomposition at 230°. Raman-active fundamentals are observed at 739, 657, 334, 325, 236, 169, 160, 120, 82, and 62 cm^{-1}. Preliminary normal-coordinate calculations by Professor R. C. Taylor of this department indicate that the expected eleventh fundamental (asymmetric $GeBr_3$ rock), which should appear near 30 cm^{-1}, is buried under the excitation line.

The absence of protonic impurities in $GeBr_2$ noticeably improves the yields of "carbenoid" products when allowed to react with unsaturated compounds.[9] We have consistently obtained yields of 1,1-dibromo-1-germacylcyclopentene-3 (II) as high as 81% using $GeBr_2$ prepared as described above in eq 5. In contrast, Gar and Mironov[2] reported the formation of a considerable amount of polymer and only a 28% yield of II using $GeBr_2$ prepared from the hydroxide and hydrobromic acid. Instead of polymer formation, we observed a small amount of 4-methyl-4-tribromogermylpentane-2-one (III) (τ 7.30, 7.83, 8.47; area ratio 2:3:6; mp 63–64°; ν_{CO}, 1670 cm^{-1}) from the reaction of $GeBr_2$ with the acetone solvent.[10]



II

(5)



$$(CH_3)_2\underset{\substack{|\\GeBr_3}}{C}CH_2\overset{\substack{O\\\|}}{C}CH_3$$

III

The facile synthesis of germanium dibromide reported here should aid investigations of the interesting reactions of divalent germanium.

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Correspondence

The Character of the Metal Atoms in Platinum–Tin Cluster Compounds

Sir:

The oxidation states of metal atoms in cluster compounds are often not apparent from inspection of the molecular formulas. There has been much discussion about the oxidation state of tin in the clusters formed by interaction of platinum chlorides with stannous chloride. Many spectral techniques including ^{119}Sn Mössbauer spectra[1-3] (nuclear γ-resonance) and far-infrared spectra[4] have been used to diagnose the electronic character of the metal atoms. Despite some conflicting results,[1,2] it appears that coordination of an $SnCl_3^-$ ion to a metal atom forms a covalent bond and the tin becomes formally tetravalent, just as in $SnCl_4$.

The question of oxidation state is even more acute in compounds based on the trigonal bipyramidal Pt_3Sn cluster.[5,6] Chemical evidence[5] suggested that the platinum atoms in this unit were *formally* zerovalent in both $[Pt_3Sn_8Cl_{20}]^{4-}$ and (1,5-cyclooctadiene)$_3Pt_3Sn_2Cl_6$. This formulation gave a plausible oxidation state of 2+ for tin in the ionic compound but resulted in a nonintegral oxidation state in the olefin complex.

TABLE I
X-RAY PHOTOELECTRON SPECTRA OF PLATINUM AND TIN COMPLEXES

Compound[d]	Binding Energy[a,c] $Pt\ 4f_{7/2}$	$Sn\ 3d_{5/2}$
$[(C_2H_5)_4N]_4[Pt_3Sn_8Cl_{20}]$	72.9	487.3[b]
$(C_8H_{12})_3Pt_3Sn_2Cl_6\cdot CH_3NO_2$	73.2	487.3
$[(C_2H_5)_4N]_3[Pt(SnCl_3)_5]$	73.2	487.1[b]
$[(C_2H_5)_4N]_2[SnCl_6]$	...	486.3
$[(C_2H_5)_4N][SnCl_3]$	...	485.7

[a] Electron volts, calibrated to a C_{1s} binding energy of 285.0 eV to compensate for charging effects. [b] The signals due to the two types of tin environments in the complex were not resolved. However, the peak widths in these two compounds were significantly greater than the 2.05 eV peak width observed for mononuclear tin compounds. [c] Spectra were determined on a Varian IEE-15 spectrometer with an Al source; estimated error ±0.1 eV. [d] Complexes were prepared as described in ref 5 and 12.

The new tool of X-ray photoelectron spectroscopy, which has shown a good correlation between electron binding energy and oxidation state in mononuclear platinum complexes,[7,8] has now been applied to this problem. The tin $3d_{5/2}$ binding energies (Table I) are

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consistent with a formal oxidation state of 4+ as proposed from Mössbauer spectra.[1,9,10] The platinum $4f_{7/2}$ binding energies for both Pt_3Sn_2 cluster compounds fall well within the range of 72.4–73.9 eV reported by Riggs[8] for 18 Pt compounds of oxidation state 2+. (This range does not overlap those of Pt complexes with oxidation states of 0 and 4+.) Thus, the platinum atoms in these clusters should be regarded as divalent rather than zerovalent if an assignment of oxidation state must be made. The assignment is quite arbitrary; a molecular orbital treatment of the cluster provides a better representation.[11]

The platinum $4f_{7/2}$ binding energy of 73.2 eV for the $[Pt(SnCl_3)_5]^{3-}$ anion[12] likewise indicates an oxidation state of 2+ for the platinum and suggests that there is little accumulation of negative charge on the central metal atom. The similarity of Pt environments in this complex and in the cyclooctadiene complex is consistent with the postulate[13] that the $SnCl_3$ ligand is like an olefin in being able to accept electron density from a metal through π-bonds.

Acknowledgment.—The author is deeply indebted to Dr. W. M. Riggs for determination of the spectra and for permission to quote his results prior to publication.

(9) As pointed out by a reviewer, a correlation between Mössbauer chemical shifts and 4d binding energies has previously been noted.[10] It is quite reasonable that a similar correlation with the 3d energies should exist.

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RECEIVED MAY 14, 1971

On the Detailed Nature of the Six-Coordinate Polyhedra in Tris(bidentate ligand) Complexes

Sir:

Recently there have been a significant number of reports of six-coordinate geometries other than the classical octahedron. Starting in 1965 there have been seven reports of full X-ray crystallographic investigations of molecular complexes wherein a nearly perfect trigonal-prismatic coordination obtains. In three[1-3] the trigonal-prismatic coordination is clearly enforced by overwhelming ligand structural and steric effects. However, the remaining four structures are of tris(1,2-dithiolate)[4-6] or tris(1,2-diselenate)[7] complexes where overriding steric requirements are not apparent and at least a partial electronic structural explanation for the stabilization of the trigonal prism must be sought.[8-10] Additionally, recent reports described geometries presumably between octahedral and prismatic limits.[11-13] In many cases the detailed nature of the coordination polyhedron was not adequately described. For example, the term "trigonally distorted octahedron" is often used to describe a tris(bidentate ligand) complex without specifying the nature of this distortion. Thus, twisted, compressed, and elongated structures (*vide infra*) have each been referred to as trigonally distorted octahedra. It is the purpose of this correspondence to (a) compare in detail the octahedral and trigonal-prismatic coordination geometries, (b) clearly describe the nature of the distortions which occur in trichelated six-coordinate complexes, and (c) assess the constraint placed on the coordination geometry by rigid bidentate ligands whose bite is more or less fixed by the organic part of the chelate. In this respect we show that many of the known structures can be looked upon as minimally distorted from a regular octahedron with the distortion attributable solely to the short bite of the ligand.

An octahedron can be viewed as a special case of the D_{3d} trigonal antiprism, which occurs when two perfectly staggered equilateral triangles of side s are exactly $\sqrt{2/3}\,s$ apart. Distortions (which maintain at least D_3 symmetry) can be broken down into two components: (1) a component which twists the triangles with respect to each other and (2) a component which changes the ratio of the side of the triangle to the distance between the triangles. The angle ϕ as defined in Figure 1a is a measure of the amount of twisting which has occurred and by precedent is set equal to 60° for the undistorted octahedron. The second type of distortion can be described by the ratio s/h where, as shown in Figure 1b, h is the distance between the parallel equilateral triangles. This ratio is a measure of the extent to which the distorted figure is compressed or elongated with respect to the regular octahedron where $s/h = \sqrt{3/2} = 1.22$. A ratio larger than 1.22 indicates a compressed structure while a

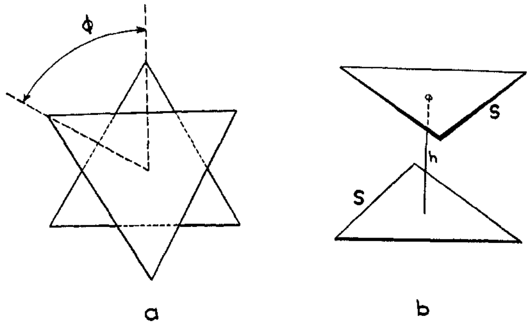

Figure 1.—(a) View of the polyhedron down the C_3 axis illustrating the angle ϕ. (b) View of the polyhedron illustrating the intertriangle distance h and the triangle side s.

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