

The great resistance of InPcCl to hydrolysis is striking in view of the relative lack of resistance of AlPcCl and GaPcCl to hydrolysis. However, it does find a parallel in the behavior of chloroindium octaethylporphyrin.³⁵

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Registry No. AlPcCl, 14154-42-8; AlPcF, 74018-71-6; AlPcBr, 18130-73-9; AlPcI, 74381-36-5; GaPcCl, 19717-79-4; GaPcF, 74018-73-8; InPcCl, 19631-19-7; phthalonitrile, 91-15-6; aluminum trichloride, 7446-70-0; quinoline, 91-22-5; AlPcOH, 15554-15-1; AlPcOSi(C₆H₁₃)₃, 74381-37-6; gallium trichloride, 13450-90-3; GaPcOH, 63371-84-6; indium trichloride, 10025-82-8.

(35) Buchler, J. W. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. I, Part A, Chapter 10.

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Oxidation State, Valency, and Electron Configuration of Tin in a Linear S-Sn-S Array

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¹¹⁹Sn Mössbauer-effect measurements have been carried out at 4.2 K in the presence of external magnetic fields of 0, 50, and 80 kOe on the intercalation compound TaS₂·Sn. The variation of the magnetic hyperfine interaction at the Sn nuclei with applied magnetic field confirms the observation (based on magnetic and ESCA data) that there is no significant unpaired electron density localized on the metal atom. The observed isomer shift of 3.2 mm s⁻¹ at 78 K is comparable to that noted in covalent Sn²⁺ compounds. The stacking of the TaS₂ matrix leads to a linear coordination of tin by two sulfur atoms from adjacent layers. The total coordination of tin—including six nearest-neighbor metal atoms in the van der Waals gap—is eight. Presumably it is the p_z and d_{z²} orbitals of tin which are involved in the bonding interaction of the linear S-Sn-S array.

2H tantalum sulfide is a layered compound having many interesting physical and chemical properties including the ability to intercalate a number of metal atoms and organic molecules in the van der Waals layer. Typical of such intercalation compounds is TaS₂·Sn,¹ for which detailed ¹¹⁹Sn Mössbauer,² ESCA,³ and magnetic susceptibility¹ studies have been reported. A definitive crystallographic structure study of this material by Eppinga and Wieggers⁴ showed that the tin atom is linearly coordinated by two sulfur atoms of the TaS₂ structure adjacent to the (hexagonal) tin layers. The space group is *P6₃/mmc*. In the earlier Mössbauer studies^{1,2} of TaS₂·Sn (and of the isostructural NbS₂·Sn⁵), the isomer shift of the intercalated tin atom (3.2 mm s⁻¹ at 78 K) was interpreted as indicating the presence of the metal atom as Sn²⁺,² although this value is less positive than that usually associated with an "ionic" stannous ion for which the isomer shifts lie⁶ in the range 3.5–4.5 mm s⁻¹. A linear S-Sn-S array would be an unusual example of such a geometry for a tin atom formally in the divalent state, for which the most common arrangement of nearest-neighbor atoms is that of a distorted 7- or 9-coordinate polyhedron, as, for example, in SnCl₂⁷ and SnI₂.⁸ Since the tantalum atom requires only a single electron to fill the d_{z²}, or lower d, band, the possibility remains that the linear S-Sn-S array may be formally ascribed to Sn⁺, rather than to the stannous state, and that the Mössbauer isomer shift value is, in fact, a reflection of an electron configuration (core) (5s)¹(5p)² or (5s)²(5p)¹, rather than that normally ascribed to divalent tin. In an attempt to examine this possibility further and to elucidate the appropriate electronic description of the tin atom in the linear S-Sn-S array in TaS₂·Sn, additional Mössbauer-effect measurements on this material have been carried out in the present study. In particular, the effective magnetic field at the Sn nucleus has been

examined as a function of the strength of an externally applied field.

Experimental Section

A sample of 2H TaS₂·Sn, identical with that used in the crystallographic studies, was generously made available to us by Dr. G. A. Wieggers of the Materials Science Center of the University of Groningen. High-field ¹¹⁹Sn Mössbauer experiments were carried out at 4.2 K on a sample prepared by dispersing the powdered microcrystalline powder in boron nitride, at the National Magnet Laboratory facility at MIT. Measurements at 0, 50, and 80 kOe were effected in transmission geometry in the core of a superconducting magnet with the field direction parallel to the optical (γ ray) axis of the experiment.

Results and Discussion

The high-field ¹¹⁹Sn Mössbauer spectra at liquid-helium temperature consist of a four-line pattern, since the Δ*m* = 0 resonance is suppressed due to the parallel orientation of the magnetic field and the direction of the Mössbauer γ rays. The energy difference between the two outer lines of the spectrum is given by

$$\Delta E = (g_0 - 3g_1)\mu_N H_n$$

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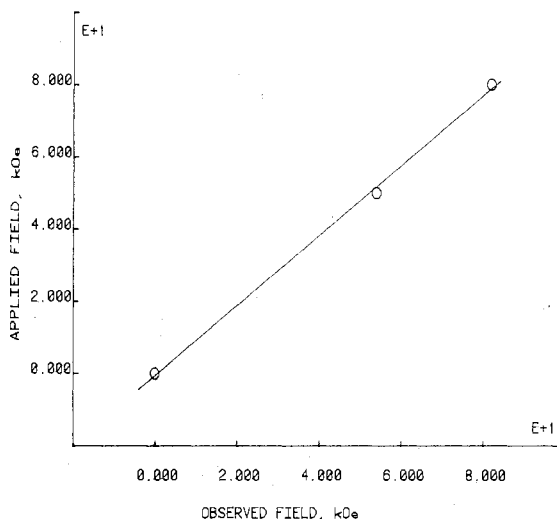


Figure 1. Observed magnetic hyperfine splitting in TaS_2Sn at 4.2 K as a function of applied field. The extrapolation of the 50 and 80 kOe values to zero applied field show that there is no contribution to the hyperfine field from unpaired electron spins in the solid.

where g is the nuclear g factor, μ_N is the nuclear magneton, and H_n is the magnetic field at the nucleus. For ^{119}Sn , the nuclear ground-state and excited-state magnetic moments are -1.041 and $+0.67 \mu_N$, respectively. Since $g = \mu/I$, the energy difference between the two outer lines of the Mössbauer spectrum becomes

$$\Delta E = [-2.082 - 3(0.417)]\mu_N H_n$$

For ^{119}Sn , this equation can be rewritten in velocity units in the form

$$\Delta v/H = -3.422(3.958 \times 10^{-2} \text{ mm s}^{-1} \text{ kOe}^{-1})$$

The magnetic field at the nucleus is given by $H_n = H_o \pm H_u$ where H_o is the externally applied field and H_u is the hyperfine field at the nucleus due to unpaired electron spins. In the absence of unpaired electrons ($H_u = 0$), the expected Doppler velocity differences in the outside line positions are ~ 6.8 and 10.8 mm s^{-1} at 50 and 80 kOe, respectively. The experimentally observed Doppler velocity differences in the two spectra are 7.4 and 11.1 mm s^{-1} , respectively, corresponding to a magnetic field at the nucleus of 54 and 82 kOe in the two cases. These data are summarized graphically in Figure 1. The slope of the three-point linear regression (using the zero-field datum) is 0.969, from which it is seen that, within the experimental errors of the measurements, the value of H_n is equal to H_o , and hence $H_u = 0$. This result precludes the presence of an electron spin moment localized predominantly on the tin atom. Indeed, a local magnetic moment arising from unpaired electrons on a post transition metal atom in a solid-state compound would have been quite unusual. Moreover, previous magnetic susceptibility measurements¹ have shown that TaS_2Sn is weakly diamagnetic over a wide temperature range, precluding the possibility of a localized magnetic moment in this compound.

These results do not, however, directly settle the question of the valence state of tin in TaS_2Sn . If the Sn transfers only one electron to the TaS_2 layer as is suggested by ESCA measurements,³ the odd electron (at least) must be paired in a metallic or covalent bond. Indeed it should be noted that the Sn-Sn distance in the intercalation layer⁴ is 3.307 \AA , a

value somewhat greater than the near-neighbor distance in tetragonal Sn (two at 2.96 \AA and two at 3.18 \AA) but short enough for significant metallic Sn-Sn bonding to occur. This metal-metal bonding interaction via the use of sp^2 hybrids would involve the six nearest-neighbor Sn atoms in TaS_2Sn , resulting in a half-filled band. This half-filled band is presumably associated with the observed metallic conductivity and superconductivity at $T_c = 2.95 \text{ K}$.^{1,4} In chemical terms, the sp^2 bonds utilize all three of the remaining electrons on Sn and can be thought of as resonating between two equivalent positions 60° apart. Due to the electronegativity differences between tin and sulfur, the bonding of the Sn to the TaS_2 layer will be partly ionic and partly covalent. The covalent part comes about through use of the empty p_z and d_z orbitals of the Sn which are directed toward the sulfur atoms. The sulfur atoms in TaS_2 have a lone pair of electrons (the van der Waals pair), which in the unintercalated compound are directed into the gap and in TaS_2Sn are oriented toward the tin atom. Using the p_z and d_z orbitals, the tin atom can form a pair bond to two sulfur atoms lying above and below the tin atom plane.

In summary, the bonding of the tin atom to its nearest neighbor can be described as involving three sp^2 -hybrid orbitals in bonding to the other tin atoms in the equatorial (van der Waals layer) plane and the p_z and d_z orbitals in bonding to the axial sulfur atoms above and below this plane to form a local trigonal-bipyramidal arrangement of atoms bonded to Sn. This type of local symmetry¹⁰ is, of course, not unique in TaS_2Sn since in many organometallic compounds—for example $(\text{CH}_3)_3\text{SnF}$,¹¹ $(\text{C}_6\text{H}_5)_3\text{SnNCS}$,¹² and $(\text{C}_6\text{H}_5\text{CH}_2)_3\text{Sn}(\text{OCOCH}_3)$,¹³ inter alia—the sp^d hybridization of the tin atom bonding orbitals is known to give rise to trigonal-bipyramidal configurations around the metal atom. Such compounds usually have ^{119}Sn isomer shifts¹⁴ (with respect to SnO_2) of 1.1 – 1.3 mm s^{-1} , that is, significantly smaller than the value observed in TaS_2Sn , implying a significantly larger s-electron density at the Sn nucleus in the intercalation compound than in the organometallic compounds. This observation can be rationalized on the basis of the greater ionicity of the Sn-S bond in TaS_2Sn which may be assumed to afford a significant deshielding effect on the 5s-electron density.

A correlation between the ^{119}Sn isomer shift and the 5s- and 5p-electron population has been proposed by Flinn¹⁵ and is of the form

$$\text{IS} = -0.45 + 3.10n_s - 0.20n_s^2 - 0.17n_s n_p$$

where the isomer shift, in mm s^{-1} , is with respect to BaSnO_3 at room temperature, and n_s and n_p are the 5s- and 5p-electron populations, respectively. If the above 5p-hybridization model is correct, it follows that

$$n_s = 3.10 \pm \left[3.10^2 - \frac{4(0.45 + 3.03)(0.37)}{0.74} \right]^{1/2}$$

from which $n_s = 1.34$. The difference between this value and 2 is, again, a reflection of the degree of covalency of the chemical bond holding the tin atom in the van der Waals layer

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(10) See, for example, Y. K. Ho and J. J. Zuckerman, *J. Organomet. Chem.*, **49**, 1 (1973), and references to structural studies therein.

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(15) P. A. Flinn in "Mössbauer Isomer Shifts", G. K. Shenoy and F. Wagner, Eds., North-Holland Publishing Co., Amsterdam, 1978, p 598.

lattice site. The value of the effective 5s-electron density around the tin atom is in consonance with the characterization of the metal atom as being formally in the stannous state, which should not, however, be taken to imply the existence of Sn^{2+} ions in this structure.

From the above description of the bonding involving the tin atom in $\text{TaS}_2\text{-Sn}$, it will be clear that the oxidation state is simply a formality which has no real meaning in such compounds. Operationally, the ^{119}Sn isomer shift value suggests that the 5s-electron density at the tin nucleus is not very much different from what is observed in covalent "stannous" compounds. The trigonal-bipyramidal bonding to the five nearest-neighbor atoms, on the other hand, is similar to that encountered in organotin species, especially those in which a bridging ligand can give rise to a linear array of (planar) trialkyltin moieties. In such compounds, the tin atom is frequently considered to be formally in the "zerovalent" state. In the case of $\text{TaS}_2\text{-Sn}$, the formal oxidation state of the tin atom can only be described in purely phenomenological terms and has no fundamental significance in describing the elec-

tronic environment around the Sn atom.¹⁶

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Registry No. $\text{TaS}_2\text{-Sn}$, 52953-71-6; ^{119}Sn , 14314-35-3.

- (16) After this paper was submitted for publication Dr. G. A. Wiegers communicated to us the fact that a different interpretation describing the bonding in TaS_2 intercalates had been developed in the thesis work of R. Eppinga, Groningen, Feb 1980. In this description, the s orbital of the post transition metal is presumed to participate in the bonding with the TaS_2 sandwich, rather than involving sp^2 hybrid orbitals in the x-y plane. This work is to be published.

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Aryldiazenido, Aryldiazene, and Arylhydrazido Complexes. NMR and IR Spectroscopic Characterization of "End-On"- and "Side-On"-Bound Arylhydrazido Ligands Formed by Insertion of the Arenediazonium Ion into a W-H Bond in $(\eta^5\text{-C}_5\text{H}_5)_2\text{WH}_2$

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The hydride Cp_2WH_2 ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) in toluene reacts with equimolar $[\text{ArN}_2][\text{X}]$ ($\text{Ar} = \text{Ph}$, $p\text{-FC}_6\text{H}_4$, $p\text{-MeC}_6\text{H}_4$, or $p\text{-MeOC}_6\text{H}_4$; $\text{X} = \text{BF}_4$ or PF_6) in methanol below ca. -20°C to give yellow salts **1** of composition $[\text{Cp}_2\text{WH}(\text{NNHAr})][\text{X}]$. These have been fully characterized by IR and ^1H NMR (with ^{15}N isotopic substitution) to contain the formally arylhydrazido(2-) ligand bound to W through N(1). Temperature dependence of the ^1H NMR of the Cp groups shows the cation to be nonrigid, and this is interpreted to be due to a rotation of the plane of the hydrazido(2-) ligand molecular skeleton into the plane bisecting the angle subtended at the W atom by the Cp groups (the Cp_2W "midplane"). The stereochemistry of the arylhydrazido(2-) ligand and its orientation in the ground state are examined. Repeating the synthesis at ca. 0°C or stirring solutions of **1** near this temperature produces an isomeric product **2** of composition $[\text{Cp}_2\text{W}(\text{H}_2\text{NNAr})][\text{X}]$ which is an arylhydrazido(1-) complex in which the ligand is bound to W through both nitrogen atoms. The IR and ^1H NMR (with ^{15}N isotopic substitution) are discussed by comparison with the X-ray crystallographically determined structure reported elsewhere.

Introduction

It is now some 12 years since Parshall first demonstrated the ability of arenediazonium ions to apparently insert into the Pt-H bond in $\text{PtHCl}(\text{PEt}_3)_2$ and suggested that the resulting aryldiazene ligand might be an analogue of one hypothetical dinitrogen hydride intermediate in the mechanism of biological nitrogen fixation.¹ In the intervening years, considerable refinement has occurred in our understanding of the nitrogen-fixing enzyme nitrogenase² and, in particular, direct synthesis of molybdenum- and tungsten-bound dinitrogen hydrides by the protonation of coordinated dinitrogen in one or two specific complexes of Mo and W has been achieved.³ Despite this progress we have, as yet, only a primitive knowledge of the chemistry of dinitrogen hydride ligands, their electronic and geometrical features, the possible rearrangements they may undergo, their coordinating ability, their reactions, and their part in biological nitrogen fixation.

Until improved and more general methods for their synthesis become available, one alternative is to examine dinitrogen hydride ligands stabilized by the presence of an organic group, and some examples of these are conveniently synthesized from arenediazonium ions and suitable hydrido complexes as Parshall showed. Though the chemistry thus identified necessarily has diminished relevance to actual biological nitrogen fixation, it is an important foundation for the development of systems in which transition-metal complexes activate molecular nitrogen for the synthesis of organonitrogen compounds. Here, we report that the apparent insertion of an arenediazonium ion into one W-H bond in Cp_2WH_2 ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) does not yield an aryldiazene ($\text{ArN}=\text{NH}$) complex but gives instead the complex ion $[\text{Cp}_2\text{WH}(\text{NNHAr})]^+$ (**1**) which formally contains an arylhydrazido(2-) ligand. This complex rearranges in solution and in the solid state to give $[\text{Cp}_2\text{W}(\text{H}_2\text{NNAr})]^+$ (**2**) in which now an arylhydrazido(1-) ligand is bound side-on to the tungsten through both nitrogen atoms. A preliminary report of this work has been published.⁴ In no instance have we been successful in duplicating, in these

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