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Nuclear Magnetic Resonance Spectra of Methylgermanium and Methyltin Halides, Oxides, Sulfides, and Selenides

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N.m.r. spectroscopic investigations on *t*-butyl halides[1] and trimethylsilyl halides, oxide, sulfide, and selenide[2] have shown that proton signals of these compounds are shifted to lower field with increasing atomic radii of the halogen or chalcogen ligands, and a systematic increase of the coupling constants $J(^1H-^{13}C)$ and $J(^1H-C-^{29}Si)$ was observed following the same sequences.[2] These relations were in contradiction to the results compiled for methyl and silyl halides[3,4] and were therefore attributed to hyperconjugation[1] and $d\pi-p\pi$-bonding effects.[2]

In a recent study we have found, however, the same correlations for analogous compounds of germanium and tin as for the carbon and silicon derivatives: Proton resonances of the compounds are shifted to lower fields with increasing atomic radii of the substituents and $J(^1H-^{13}C)$ coupling constants increase in each series in this direction (F → I, O → Se).[5]

These findings for compounds having the third- and fourth-row elements germanium and tin as central atoms can no longer be interpreted in terms of hyperconjugation or π-bonding, since these concepts are not likely to play an important role in the bonding of these elements. For the same reasons (namely, the large atomic radii), steric factors should not be important. This leads to the suggestion that most of the correlations observed for these derivatives of carbon, silicon, germanium, and tin must be ascribed mainly to some other common effect, most likely the anisotropy or dispersion effect of the ligands.[1,6] It is not yet possible to estimate the contributions from π-bonding or hyperconjugation to the observed n.m.r. data and a good deal of further investigation will be required to answer these questions, although these concepts of chemical bonding have already obtained significant support from quite a number of other chemical and physical sources.[7]

Table I

Chemical Shifts, δ, and Coupling Constants, J, of Trimethylgermanium Halides, Oxide, Sulfide, and Selenide[a]

	δ, c.p.s.	$J(^1H-^{13}C)$, c.p.s.	$J(^1H-^{19}F)$, c.p.s.
$(CH_3)_3GeF$	−30.6	128.8	6.8
$(CH_3)_3GeCl$	−46.6	128.3	...
$(CH_3)_3GeBr$	−52.8	129.2	...
$(CH_3)_3GeI$	−59.0	129.8	...
$[(CH_3)_3Ge]_2O$	−18.5	125.5	...
$[(CH_3)_3Ge]_2S$	−32.0	127.4	...
$[(CH_3)_3Ge]_2Se$	−40.0	127.1	...

[a] Varian A60, 60 Mc., room temperature. All substances in CCl_4 solution with concentrations of 3 ± 1% (v./v.), tetramethylsilane as internal standard of comparable concentration. All values in c.p.s.; negative values are supplied for the low-field side of the standard. Standard deviations are ±1 c.p.s. for δ, $J(^1H-^{13}C)$, and $J(^1H-^{117,119}Sn)$, ±0.1 c.p.s. for $J(^1H-^{29}Si)$.

Table II

Chemical Shifts, δ, and Coupling Constants, J, of Trimethyltin Halides, Oxide, Sulfide, and Selenide[a]

	δ, c.p.s.	$J(^1H-^{13}C)$, c.p.s.	$J(^1H-^{117}Sn)$, c.p.s.	$J(^1H-^{119}Sn)$, c.p.s.
$(CH_3)_3SnF$	...		Insoluble	
$(CH_3)_3SnCl$[b,c]	−37.6	133.0	56.1	58.5
$(CH_3)_3SnBr$[c]	−44.2	134.0	55.8	58.4
$(CH_3)_3SnI$	−53.0	134.0	55.6	58.0
$[(CH_3)_3Sn]_2O$	−14.2	128.8	53.6	56.0
$[(CH_3)_3Sn]_2S$	−23.8	130.8	53.9	56.3
$[(CH_3)_3Sn]_2Se$	−34.5	132.0	53.5	56.0

[a] See footnote *a*, Table I. [b] J. R. Holmes and M. D. Kaesz, *J. Am. Chem. Soc.*, **83,** 3903 (1961). [c] G. P. van der Kelen, *Nature*, **193,** 1069 (1962).

Table III

Chemical Shifts, δ, and Coupling Constants, J, of Hexamethylheterosilthianes[a]

	δ_{Si}, c.p.s.	$J(^1H-^{13}C)$, c.p.s.	$J(^1H-^{29}Si)$, c.p.s.	δ_X, c.p.s.	$J(^1H-^{13}C)$, c.p.s.	$J(^1H-^{117,119}Sn)$, c.p.s.
$(CH_3)_3SiSSi(CH_3)_3$	−19.5	119.5	6.9	−19.5	119.5	...
$(CH_3)_3SiSeGe(CH_3)_3$[b]	−18.8	120.0	6.9	−33.5	127.6	...
$(CH_3)_3SiSSn(CH_3)_3$[c]	−17.4	120.0	6.8	−26.6	131.0	57.0/53.8

[a] See footnote *a*, Table I. [b] I. Ruidisch and M. Schmidt, *Chem. Ber.*, **96,** 1424 (1963). [c] I. Ruidisch, unpublished.

The relations reported for hexamethylheterosiloxanes $(CH_3)_3SiOX(CH_3)_3$ (X = Si, Ge, Sn, Pb)[2] should

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(1) A. A. Bothner-By and N. C. Naar-Colin, *J. Am. Chem. Soc.*, **80,** 1728 (1958).

(2) H. Schmidbaur, *ibid.*, **85,** 2336 (1963).

(3) A. L. Allred and E. G. Rochow, *ibid.*, **79,** 5361 (1957).

(4) (a) E. A. V. Ebsworth, "Volatile Silicon Compounds," Pergamon, Oxford, 1963, pp. 22–26; (b) E. A. V. Ebsworth and J. J. Turner, *J. Phys. Chem.*, **67,** 805 (1963).

(5) The spin–spin interactions $^1H-C-^{117,119}Sn$ remain almost constant within the limits of the experimental errors, which are somewhat greater here than for the $J(^1H-C-^{29}Si)$ values. An interaction $^1H-C-^{73}Ge$ could not be detected in germanium derivatives of this type, having low valence symmetry around the metal atom, because of the high quadrupole and spin moment of this ^{73}Ge isotope.

(6) T. Schaefer, W. F. Reynolds, and T. Yonemoto, *Can. J. Chem.*, **41,** 2969 (1963).

(7) Reference 4a, p. 156 ff.

be less susceptible to anisotropy effects because of the presence of the same chalcogen ligand in all of the four compounds, and their validity is now supported by our results from studies on the analogous thio compounds of the type $(CH_3)_3SiSX(CH_3)_3$.

For the sequence with X = Si, Ge, Sn the proton signals of the $(CH_3)_3Si$– group are shifted to higher fields, whereas the $(CH_3)_3X$ signals appear at the low-field side with respect to the signals of the related $[(CH_3)_3X]_2S$ compounds.[2] Simultaneously, as in the case of the oxygen derivatives, the coupling constants $J(^1H-^{13}C)$, $J(^1H-^{29}Si)$, and $J(^1H-^{117,119}Sn)$, respectively, are increased in $(CH_3)_3X$ and decreased in $(CH_3)_3Si$, but obviously the effects for δ and J are in all cases smaller than in the $(CH_3)_3SiOX(CH_3)_3$ series, and are, as for $J(^1H-^{13}C)$ of $(CH_3)_3Si$, within the standard deviations of the experiment. The suggestion that these values (Table III) are reflecting the weaker π-interactions between sulfur and the group IVb elements rather than between oxygen and these elements (particularly with silicon) should remain open for discussion.

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CONTRIBUTION FROM THE PIGMENTS DEPARTMENT,
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Preparation and Properties of Some Novel Rare Earth Compounds of the Types $LnTi_{0.5}Mo_{0.5}O_4$ and $LnTi_{0.5}W_{0.5}O_4$

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In 1935 Beintema[1] presented evidence for a defect rare earth tungstate, $Ln_{2/3}\square_{1/3}WO_4$, of the scheelite type where $\square$ represents lattice defect sites. Later work by Sillén[2] failed to verify the structure. More recently, Nassau[3] described substituted tungstates of the type $(Ca_{1-x}Eu_x{}^{II})WO_4$, $(Ca_{1-3x}Nd_{2x}{}^{III})WO_4$, $(Ca_{1-2x}Nd^{III}Na_x{}^{+})WO_4$, $(Ca_{1-3x}Y_{3x}{}^{III})(W_{1-x}Cr_x{}^{III}O_4)$, and $Ca(W_{1-x}Cr_x{}^{VI}O_4)$, where x was generally very small. Van Uitert[4] described molybdates of the type $M^A{}_{0.5}M^B{}_{0.5}MoO_4$, where M^A = Li, Na, and K; $M^B = Y^{+3}$ and the trivalent rare earth ions or combinations thereof. Van Uitert[5] has also published a summary of the alkaline earth, alkali metal rare earth tungstates and molybdates of the scheelite type.

In this note, compounds of the type $Ln^{III}Ti^{IV}{}_{0.5}Mo^{IV}{}_{0.5}O_4$ and $Ln^{III}Ti^{IV}{}_{0.5}W^{IV}{}_{0.5}O_4$ are described and structural correlations are made. Although most of these compounds do crystallize in the "scheelite" structure, one can best consider them as IV/VI substituted niobates or tantalates of the types $Ln^{III}Nb^VO_4$ or $Ln^{III}Ta^VO_4$. Keller[6] has recently shown that most of these compounds crystallize in a monoclinic lattice of the "fergusonite" type. The compounds investigated in this study can be characterized as crystallizing in one of these two types. Extended solid solutions of scheelites and fergusonites are formed in the series $(LnM^AO_4)_x(LnM^BO_4)_{1-x}$ where $M^A = Nb^{+5}$ and Ta^{+5} and $M^B = Mo^{+6}$ and W^{+6}. The transition of one type into the other has been specifically investigated for the $EuNbO_4$–$CaWO_4$ and $YNbO_4$–$CaWO_4$ systems, to be reported in another paper.

Experimental

Tungsten oxide (99.9+%) was obtained from the Sylvania Chemical and Metallurgical Division, MoO_3 was Fisher certified reagent, and the rare earth oxides (99.9%) were obtained from the Lindsay Chemical Division. Scandium oxide was prepared from resublimed $ScCl_3$ which in turn was obtained by chlorination of thortveitite from Norsk Feldspat, Norway. High-purity TiO_2 was made from water-clear redistilled $TiCl_4$ by careful hydrolysis and subsequent sintering at 900–1000° under oxygen. The oxides of Ce, Pr, and Tb were obtained in a valence state higher than three and the true sesquioxides were prepared by hydrogen reduction at 1200°. All subsequent reactions with these three particular oxides were carried out under purified argon to prevent any reoxidation.

The component oxides were weighed to the nearest 0.1 mg. according to stoichiometry, and mixing was effected by ballmilling in a mechanical agate ballmill under acetone. In a first firing step, the dried mixture was heated to 700° for 10–14 hr. in the case of the molybdenum-containing compositions, and to 950° for the tungstates. These prereacted products were then homogenized by a second ballmilling under acetone, dried, and pressed into 1-in. diameter pellets under 20,000 to 40,000 p.s.i. In a second step, these pellets were fired at 1000–1200° for another 10–14 hr., which yielded completely reacted homogeneous preparations free of any component oxides as evidenced by the X-ray patterns. Outside of some spot analyses for Ti, Mo, or W, chemical analyses were generally not performed, since the constituent components were already of confirmed purity and weight losses during the different firing steps did not generally exceed 0.2% for 10.000-g. charges.

X-Ray Results.—All parameter determinations are based on powder patterns obtained with a 114.6-mm. Philips camera. The samples were ground to −325 mesh, sealed in 0.2-mm. Lindemann glass capillaries, and exposed to copper Kα radiation (λ = 1.5418 Å.) at 25° for 3–5 hr. The readings were taken visually at constant temperature with a Hilger and Watts film measuring rule with 0.05-mm. vernier divisions. All films were corrected for film shrinkage. The tetragonal patterns could be completely indexed on the basis of the reported $CaWO_4$ structure, ASTM file card 7-210. The a-parameter was generally derived from the (200), (220), (400), and (420) reflections and the c-parameter from (004), (327), (1.0.11.), (3.1.10), and (428). The other diagrams could be completely indexed based upon monoclinic symmetry isostructural with fergusonite, $YTaO_4$, ASTM file card 9-341. The extraction of the monoclinic lattic constants from powder data was generally based on the following six low-angle (*hkl*) reflections: (040), (200), (002), (204), (042), (202). Pycnometric densities were obtained by vacuum distilling CCl_4 onto the −200 mesh powders contained in a 5-ml. calibrated pycnometer. Lattice parameters together with the densities are summarized in Table I for the molybdates and in Table II for the tungstates.

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(4) L. G. Van Uitert, *J. Chem. Phys.*, **37**, 981 (1962).

(5) L. G. Van Uitert, *J. Electrochem. Soc.*, **107**, 803 (1960); **110**, 46 (1963).

(6) C. Keller, *Z. anorg. allgem. Chem.*, **318**, 89 (1962).